WRDC-TR-90-4130
ADA232740

Kinetic and Rheological Studies of a Model In-Situ Molecular Composite System (PAA/DNI-3A)

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January 1991

Final Report for Period April 1989 to June 1990

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION: Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; distribution is unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S): WRDC-TR-90-4130	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION: Materials Lab, WRDC, AFSC; 6b. OFFICE SYMBOL (If applicable): WRDC/MLBP	7a. NAME OF MONITORING ORGANIZATION
6c. ADDRESS (City, State, and ZIP Code): Wright-Patterson AFB OH 45433-6533	7b. ADDRESS (City, State, and ZIP Code)
8a. NAME OF FUNDING/SPONSORING ORGANIZATION; 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
61102F	2303	Q3	07

11. TITLE (Include Security Classification)
Kinetic and Rheological Studies of a Model In-Situ Molecular Composite System (PAA/DNI-3A)

12. PERSONAL AUTHOR(S)
Yih-Fang Chen and Charles Y-C Lee

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Interim	FROM Apr 89 TO Jun 90	January 1991	138

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	
07	04		
11	04		

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A model compound of In-Situ Molecular Composite system, poly(amic dialkylamide) was prepared and characterized in an attempt to better understand the rod conversion for designing a processing scheme for these materials. The conversion kinetics and the chemorheology of the system were studied by using FTIR and TICA. The activation energy was found to be higher than the values reported for poly(amic esters). The rod conversion kinetics was controlled by rheology. Two different kinetic rates were observed before and after the vitrification point. A Fixed-Time-Interval method for using FTIR data to analyze kinetic rate was developed. The effect of pressurization on the thermal behavior of the model system was analyzed. This study clearly indicated that the rod conversion chemistry is rheologically controlled.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION	
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL: Charles Y-C Lee	22b. TELEPHONE (Include Area Code): 513-255-9155	22c. OFFICE SYMBOL: WRDC/MLBP

DD Form 1473, JUN 86 — Previous editions are obsolete.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2303, "Nonmetallic and Composite Materials," Task No. 2303Q3, work unit Directive 2303Q307, "Structure Resin." It was administrated under direction of Materials Laboratory, Wright Research and Development Center, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. R.C. Evers as the Materials Laboratory Project Scientist. Coauthors were Dr. Yih-Fang Chen (Adtech System Research, Inc.) and Dr. Charles Y-C. Lee, Materials Laboratory (WRDC/MLBP). This report covers research conducted from April 1989 to June 1990.

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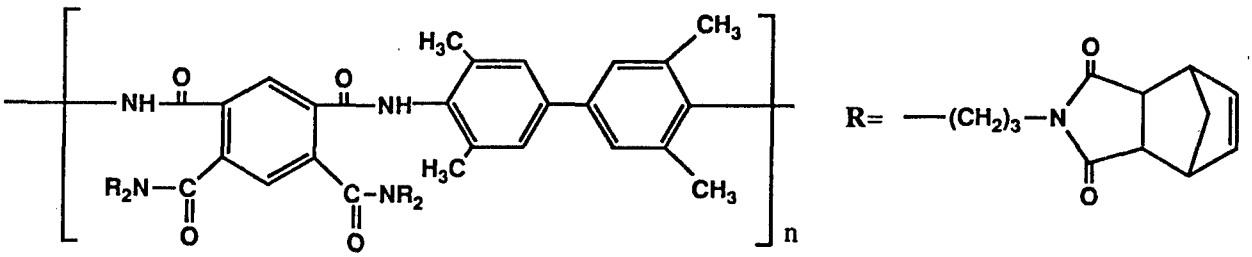
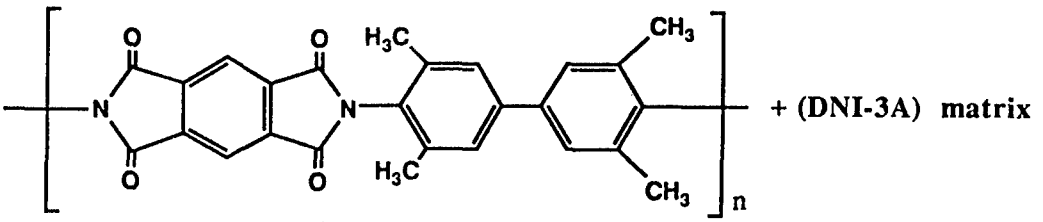
SECTION 1
INTRODUCTION

The concept of In-Situ Molecular Composites (ISMC) was introduced previously [1,2]. These ISMC systems will undergo an intramolecular thermal elimination (ring closure) to form the rigid-rod polyimide, and the evolved pendants can crosslink to form an in-situ network. The feasibility of the conversion (ring-closure only) has been proven spectroscopically [3]. However, to yield useful properties, the ISMC materials will have to consolidate, to attain complete conversion to generate high aspect ratio rods, and to remain molecularly dispersed. These factors are very much controlled by the rheology of the systems during processing. Sufficiently low viscosity is required for consolidation and rod conversion, but too low a viscosity will cause the aggregation of the rod molecules. The successful conversion of the aforementioned poly(amic dialkylamides) into molecular composites will necessitate a careful definition of the processing window.

In an attempt to understand better the process of rod conversion so as to design a processing scheme for these materials, the kinetics of rod conversion and its relationship with the rheology of a prototype system, poly(amic amide/DNI-3A) (PAA/DNI-3A) where DNI-3A is an alkyl dinadiimide derived from 3,3'-iminobispropylamine and nadic anhydride, was studied. The structure and imidization of PAA/DNI-3A is shown in Fig.1. FTIR was used to follow the degree of imide conversion. Analysis of the kinetic algorithm showed that systematic errors could be introduced if the final concentration of reactant was not accurately known. A modified fixed-time-interval approach was developed and was used to analyze the kinetic data. Chemorheology of the system was studied by using TICA



poly(amic dialkylamide)/DNI-3A



Polyimide (rigid rod)

Fig.1. Chemistry of PAA/DNI-3A for in-situ rod reinforced molecular composite

DNI-3A matrix network

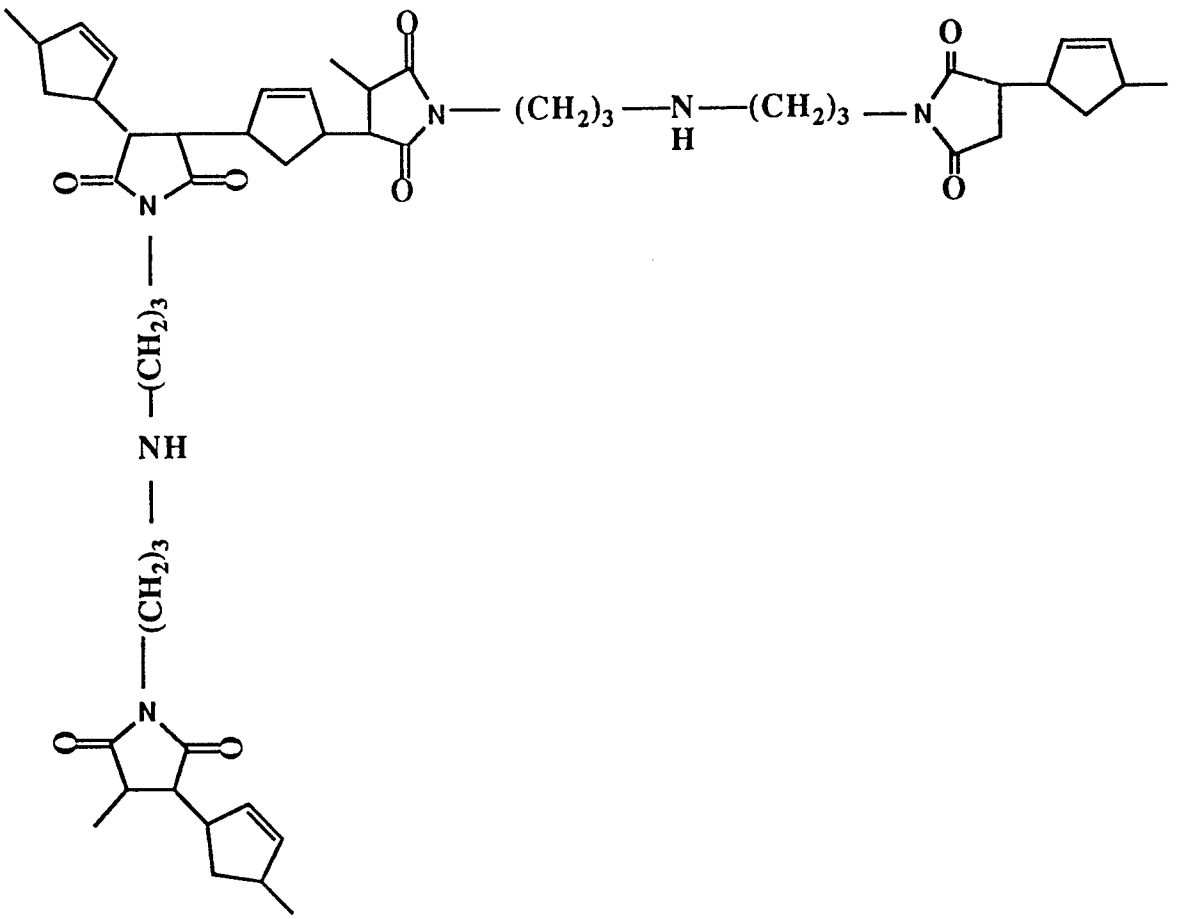


Fig.1. (continued)

in isothermal and temperature scan modes. The DSC of the model system polymer and the model leaving group under ambient and pressurized condition was analyzed.

SECTION 2

EXPERIMENTAL

The poly(amic amide) samples (PAA/DNI-3A) (sample #A90501) used in this study was prepared by Tan [1,2]. The synthesis of this compound is based on a previously published synthesis route for poly(amic dialkyl amide) [4]. The details of the synthesis of this compound will be published separately [1,2]. The syntheses reaction is summarized in Fig. 2. PMDA (pyromellitic dianhydride) and TMB (tetramethyl benzidine) as the starting monomers were reacted to yield a poly(amic amide), which was sequentially converted to polyisoimide, and finally to poly(amic dialkyl amide). The leaving group of this compound is an alkyl group terminated with norbornene.

Film samples of PAA/DNI-3A were solvent casted from 0.4% concentration DMAc solutions. About 10 ml of this solution was placed on a 3.5" petri dish. Vacuum was applied for 24 hours to remove the solvent. The film was then immersed in acetone overnight to remove residual DMAc. The film was subsequently rinsed with acetone several times and dried in air. Small pieces of the films were sandwiched between KCl plates for FTIR studies. The plates were mounted inside a temperature controlled fixture for kinetic studies.

After placing the fixture inside the IR chamber, the film was heated at the rate of about 40°C/min to the desired temperature. When the system reached a predetermined temperature, the timer was started and an initial IR scan was recorded. Subsequent spectra were recorded at appropriate time intervals. The spectra were stored in an on-line computer for later use. After the last spectrum was recorded the heater was turned off and the film was allowed to cool. The final IR scan for the cooled sample was also recorded.

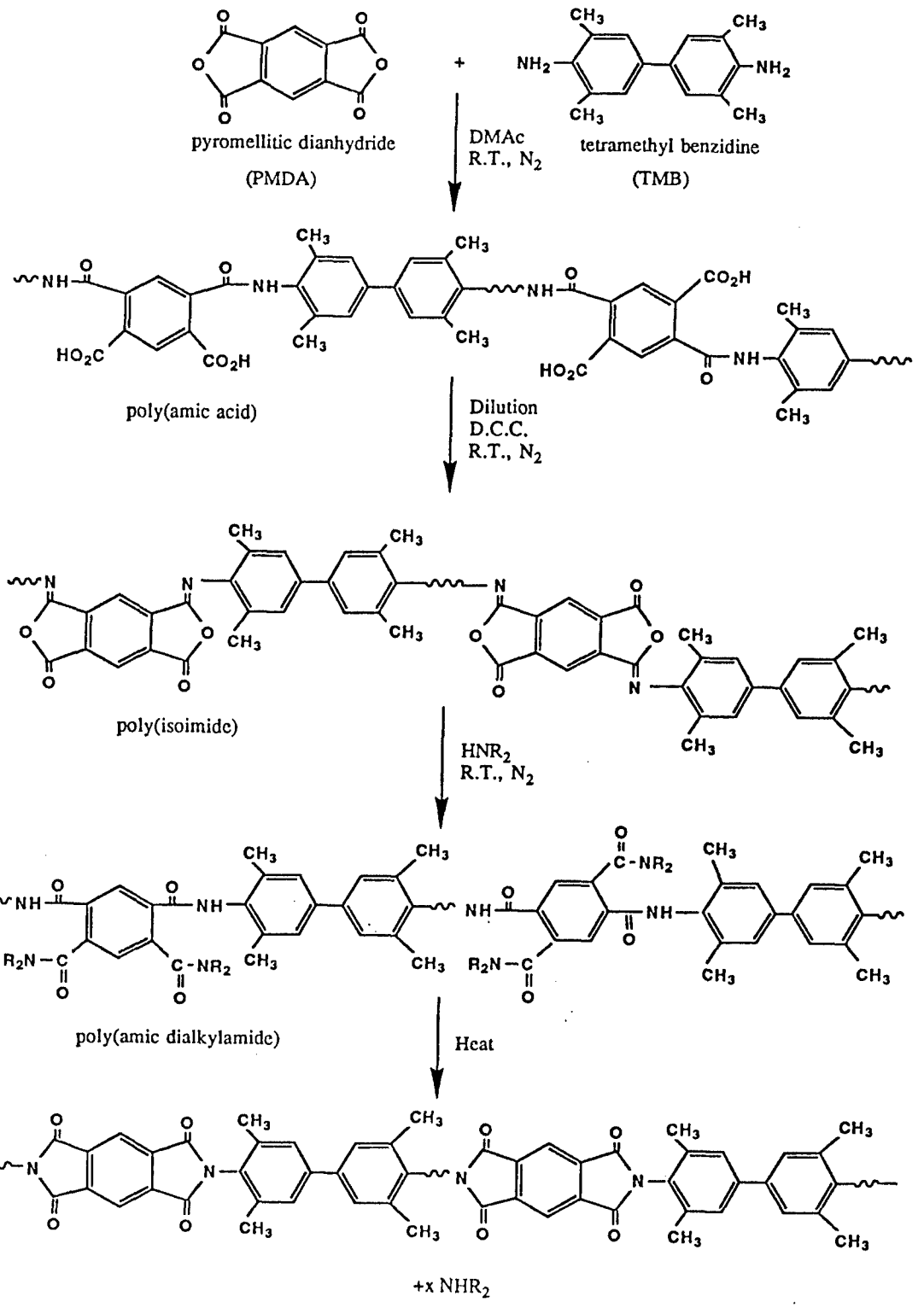


Fig.2. Synthesis route for PAA/DNI-3A and polyimide

The details of TICA specimens preparation and experimentation were described elsewhere [5]. A piece of glass cloth of 3"x4" was prepared by pulling two strands of fibers every half inch in the width direction. The cloth was immersed in a 4% DMAc solution of the polymer and placed in a desiccator for vacuuming and drying. Then the cloth was immersed in acetone overnight to remove residual DMAc. Before being dried in air the cloth was rinsed with acetone several times. The dried cloth was then cut in halves and folded into strips of 1.2 cm wide, 6.4 cm long and 0.2 cm thick, with the cut edges folded inside the strips. The specimen was made by stacking two strips with the ends sandwiched by two metal plates held together by a screw at the center. The TICA specimen was mounted on the RDS instrument with the end metal plates as fixtures. The instrument was set at "torsion" mode and the control mode was set at "cure".

SECTION 3
BACKGROUND

3.1 Possible Chemistry Description

The PAA/DNI-3A chemistry is similar to PMR-15 [6]. The monomers used in PMR-15 include a dialkyl ester of aromatic tetracarboxylic acid such as BTDE, an aromatic diamine like MDA, and a monoalkyl ester of norbornene 2,3-dicarboxylic acid (NE). They are dissolved in a low boiling alkyl alcohol. After heating to 150-220°C temperature range, the the solvent was removed and the monomers undergo in-situ condensation and cyclodehydration to yield norbornenyl end-capped low molecular weight imide prepolymer. Under pressurized condition, the end-capped prepolymer undergoes addition polymerization (crosslinking) at 260-315°C without evolution of volatiles.

The same types of reactions occur in the current PAA/DNI-3A system. The high molecular weight poly(amic amide) will undergo ring closure imidization probably at a higher reaction temperature. A leaving group with a reactive end-cap will be released from the reaction. This leaving amine group, NH(nadic-3A)$_2$, may undergo crosslinking reaction and degrade due to the instability of the alphilic bonds in its structure.

3.2 Temperature Range of the Reactions and the FTIR Measurement

The polyimide formation reactions from different prepolymers such as poly(amic acid), poly(amic ester) or poly(amic amide) are similar. Most of the data in literature were from poly(amic acid) system and in solution state. The activation energy and mechanism for the imide formation in the solution state can be different from that in the solid state. It has been shown that the solvent-polymer interaction caused difficulty in the removal of solvent in the

final stage [7,8] and affected the imidization rate [9]. The condensation reaction product, water, also induced hydrolysis of the polymer and cause rapid degradation [10].

The kinetics of the formation of imide showed that it was a first order reaction and is linearly proportional to the concentration of amic acid. Recently, a second order reaction mechanism of maleimide formation was reported [11]. It was argued that the imidization rate is proportional to the product of the amic acid concentration and the catalyst acetic anhydride concentration. Nevertheless, most reports agreed that the imide formation reaction being a first order reaction. Most of the research on imide formation kinetics were based on FTIR technique. The temperature range for the imide formation and the associated kinetic data including pre-exponent constant and the activation energy constant are listed in Table 1.

For PMR type polyimide, the crosslinking reaction of the nadic group, occurs at a higher temperature. The reaction mechanism still remains controversial. Some possible reaction routes found in the literature are shown in Fig.3 [20,21]. The crosslinking reaction of the nadic group involves a retro-Diels Alder reaction in which the nadic group cracks down to form maleimide and cyclopentadiene. The cyclopentadiene has boiling temperature about 41°C which is much lower than the crosslinking temperature. In order to incorporate the cyclopentadiene compound in the crosslinking reaction, a high pressure environment has to be maintained to suppress the evolution of pentadiene.

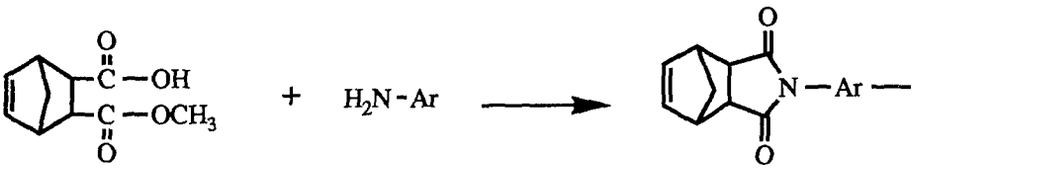
Experiments also showed this crosslinking reaction for the PMR system to be a first order reaction. The kinetic data of this reaction was determined by DSC thermoanalysis. Only one set of kinetic data was found in the literature [15], and the values are:

$A=2.5\ E15\ (min^{-1})$, $E=44\pm2$ Kcal/mole, $T=275\text{-}325°C$ with pressure.

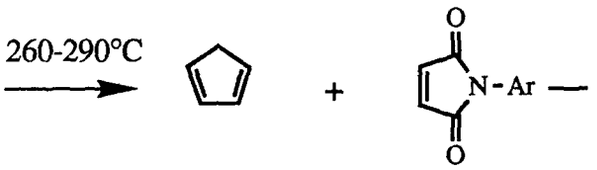
Table 1. The kinetic parameters of imdization in the literature

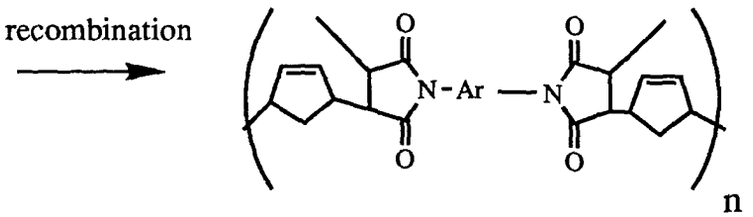
$k_0(min^{-1})$	E (Kcal/mole)	Reaction Temp (°C)	Reference
	28.2	150-200	[9]*a
	23±7 (slow) 26±3 (fast)	161-188	[12]*b
4.6 E 10	26 ± 4		[13]*c
	19.5		[14]*d
8.4 E 8	24 ± 6	120-204	[15]*e
	10 ± 1	100-170	[16]*f
	14-65	150-250	[17]*g
6.8 E 10	26	140-170	[18]*h
	8.6 ± 2.3	140-200	[19]*i
	12 (2nd order rxn)	27-80	[11]*j
*a. BTDA + DABP in diglyme solvent, by FTIR, 720 and 1780 cm^{-1}			
*b 4,4'-diaminodiphenyl ether + PMDA in DMAc solvent, by FTIR, 725 cm^{-1}			
*c, *d, dianhydride + diamine (not specified), 720 & 1380 cm^{-1} (recommended)			
*e NE + MDA + BTDE in methanol (PMR system), by FTIR, 1370cm^{-1}			
*f PMR-15 by RDS method			
*g PMDA/ODA, E=28, BTDA/ODA, E=22, BPDA/ODA, E=16, BPDA/ODA, E=14, Toray photoneece, E=26, PMDA/ODA ethyl ester, E=65, all by FTIR, 1780cm^{-1}			
*h BTDA + DDS + siloxane oligomer in NMP/CHP cosolvent for solution imidization, by FTIR, 725cm^{-1}			
*i PMDA + ODA in NMP solvent, by Fluorescence Spectroscopy			
*j Maleamic acid --> maleimide, 2nd order reaction, by 1H-NMR			

(Scola, 1985 [21])



endo or exo nadimide isomer





crosslinked polyimide

Fig.3. Possible reaction routes for nadic group

(Gaylord, 1981 [20])

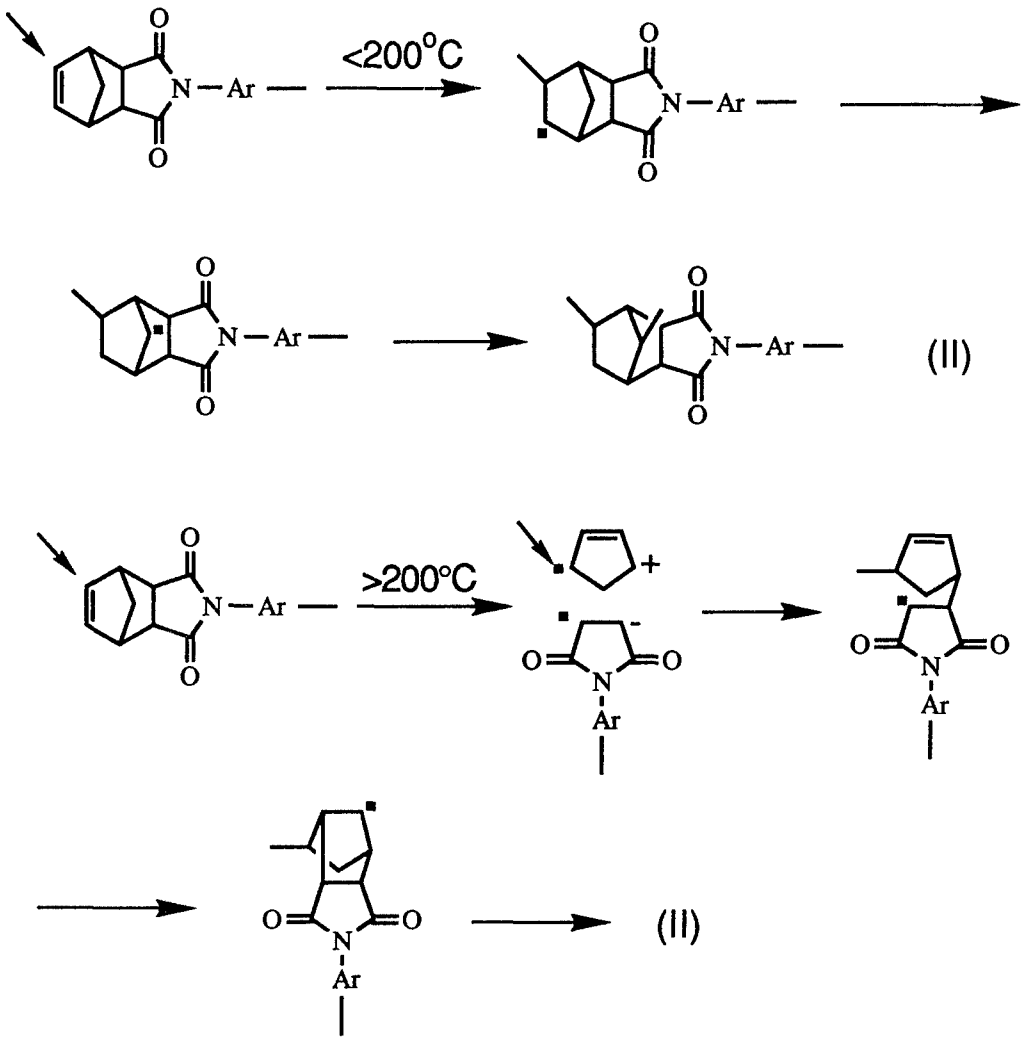


Fig.3. (continued)

Myers [16] used PMR-15 prepreg by RDS instrument to obtain the activation energy of the crosslinking reaction to be 14±2 Kcal/mole, a value much smaller than Lauver's data.

3.3 First Order Reaction Kinetics Based on Normalized Concentration

From FTIR data, the first order reaction kinetic parameters can be obtained by two methods. One is based on the reactant or product normalized concentration, and the other is based on fixed-time-interval data. These two techniques will be analyzed in detail in this and the next sections. But first let's examine the first order reaction kinetics.

The first order chemical reaction

$$C \rightarrow P$$

is represented by the following differential equation:

$$\frac{d[p]_t}{dt} = -\frac{d[c]_t}{dt} = k[c]_t \qquad (1a)$$

The initial conditions are defined as:

$$\text{i.c. } @\ t=0, [c] = [c]_0\ ,\ [p] = [p]_0 \qquad (1b)$$

The following equation holds for the first order reaction:

$$[p]_0 + [c]_0 = [p]_t + [c]_t = [p]_\infty + [c]_\infty = \text{constant.} \qquad (1c)$$

Please note that in this report the notation $[c]_\infty$ represents the reactant concentration at infinite reaction time and is therefore zero. With the conditions (1b) and (1c), the

differential equation (1a) can be solved by direct integration method to obtain the solution of $[c]_t$ and $[p]_t$,

$$[c]_t = [c]_0 e^{-kt}$$
$$[p]_t - [p]_0 = [c]_0(1 - e^{-kt}) \qquad (2)$$

For accurate determination of the first order kinetics parameters, either the initial product concentration $[p]_0$ or the final reactant concentration has to be accurately determined. In infrared spectroscopy the concentration can be extracted from the absorbance according to Beer's Law, which is,

$$\text{Beer's Law:} \qquad A = ab[c] = -\log_{10}T \qquad (3)$$

where A is the absorbance,

a is the absorptivity, [cm^2/ mole],

b is the path length, [cm],

[c] is the concentration of the absorbing species, [mole/cm^3]

T is the transmittance,

If the systems contains some inert species (an absorption peak that does not change in intensity in the course of the reaction being studied) which absorb at the same frequency, then

$$A(\nu_C, t) = A_C(t) + A_i = a_C b [c]_t + a_i b [I] \qquad (4)$$
$$A(\nu_P, t) = A_P(t) + A_{i'} = a_P b [p]_t + a_{i'} b [I']$$

where $A(\nu_c,t)$ and $A(\nu_p,t)$ are the apparent absorbance at peak frequency for C and P moieties respectively, $A_C(t)$ and $A_P(t)$ are the true absorbance of C and P at time t, A_i and $A_{i'}$ are the absorbance of inert species I and I' respectively.

In equation (4), $A_C(t)$ and $A_{pr}(t)$ are the desired quantities for the kinetic study, but $A(\nu_c,t)$ and $A(\nu_p,t)$ are the experimentally measured data. The background absorbance can be removed by subtracting different spectra:

$$A(\nu_c,t_1) - A(\nu_c,t_2) = A_c(t_1) - A_c(t_2) = a_c b\,([c]_{t_1} - [c]_{t_2}) \qquad (5)$$

$$A(\nu_p,t_1) - A(\nu_p,t_2) = A_p(t_1) - A_p(t_2) = a_p b\,([p]_{t_1} - [p]_{t_2})$$

This subtraction result is the change in absorbance as a result of the reaction. Normalizing the subtraction data with the total change between t=0 at the beginning of the experiment and $t=\tau$ at the end of the experiment, will yield

$$\frac{A(\nu_c,0) - A(\nu_c,t)}{A(\nu_c,0) - A(\nu_c,\tau)} = \frac{[c]_0 - [c]_t}{[c]_0 - [c]_\tau} \qquad (6a)$$

$$\frac{A(\nu_p,t) - A(\nu_p,0)}{A(\nu_p,\tau) - A(\nu_p,0)} = \frac{[p]_t - [p]_0}{[p]_\tau - [p]_0} \qquad (6b)$$

with

$$\frac{[c]_0 - [c]_t}{[c]_0 - [c]_\tau} = \frac{[p]_t - [p]_0}{[p]_\tau - [p]_0} \qquad (6c)$$

The ratio terms shown in equation (6c) represent the normalized degree of reaction conversion. If $[c]_\tau$ is sufficiently close to zero ($[c]_\tau \sim [c]_\infty = 0$) then the data obtained according to equation (6a) and (6b) can be analyzed by replacing τ by ∞ and using the kinetic equation (2). Thus the logarithm of $[c]_t/[c]_0$ (or $[A(t)-A(\infty)/A(0)-A(\infty)]$) versus time t plot will yield a straight line with the slope being the desired reaction constant k. But if $[c]_\tau$ is not zero, equation (6) will not be equivalent to equation (2), but instead be

$$1-\frac{A(t)-A(0)}{A(\tau)-A(0)} = \frac{A(t)-A(\tau)}{A(0)-A(\tau)} = \frac{[p]_t - [p]_\tau}{[p]_0 - [p]_\tau} = \frac{[c]_t - [c]_\tau}{[c]_0 - [c]_\tau} \neq e^{-kt} \qquad (7)$$

The logarithm of $([c]_t-[c]_\tau)/([c]_0-[c]_\tau)$ versus time t plot in this case will not give the correct quantity k. The analysis in the following section then has to be taken.

3.4 First Order Reaction Kinetics Based on Fixed-Time-Interval Data

From equation (2) one can immediately obtain the following equation,

$$\begin{aligned} [c]_{t_1} - [c]_{t_2} &= [c]_0(e^{-kt_1} - e^{-kt_2}) \\ [p]_{t_1} - [p]_{t_2} &= -[c]_0(e^{-kt_1} - e^{-kt_2}) \end{aligned} \qquad (8)$$

Equation (5) can be rewritten in the following general form,

$$\Delta A(t_1, t_2) = k' (e^{-kt_1} - e^{-kt_2}) \qquad (9)$$

where $\Delta A(t_1, t_2)$ represents either $A(c, t_1)-A(c,t_2)$ or $A(p, t_1)-A(p,t_2)$ and $k' = a_c b[c]_0$ or $-a_p b[c]_0$. Taking the logarithm of equation (9) yields

$$\begin{aligned} \ln \Delta A(t_1, t_2) &= \ln \left\{ k' (e^{-kt_1} - e^{-kt_2}) \right\} \\ &= \ln k' - kt_1 + \ln \left\{1 - e^{-k(t_1 - t_2)}\right\} \end{aligned} \qquad (10)$$

Now if $(t_1 - t_2)$ is set to be constant (equally spaced time data), equation (10) can be rewritten as

$$\begin{aligned} \ln \Delta A(t_1, t_2) &= \ln k' - kt_1 + \ln \left\{1 - e^{-k(t_1 - t_2)}\right\} \\ &= k'' - kt_1 \end{aligned} \qquad (11)$$

with k" being a constant as well.

From equation (11) with equally spaced data, the plot of [ln $\Delta A(t_1, t_2)$] verse t_1 will generate the slope (-k), which is the desired reaction rate constant at that particular temperature. The example for using these two different approaches to calculate the kinetic data are shown in Appendix A for comparison.

SECTION 4

RESULTS AND DISCUSSION

4.1 Chemistry Correlated with DSC and TGA/MS Results

To further characterize the chemistry of PAA/DNI-3A system (sample #A90501) at elevated temperature, the system was analyzed by TGA/MS spectra. The report from SRL is shown in Appendix B. The result, shown in Fig.4a, illustrated that cyclopentadiene (C_5H_6) started to evolve ~150°C as the product of the reverse Diels Alder reaction. No other product were released in this temperature range. The next volatile product started above 300°C with m/e being 138 and was assigned as $C_3H_6NC_3H_5NCO$. This is part of the secondary amine from DNI group. Fig.4b showed the TGA/MS result of the model compound, DNI-3A (also see Appendix B for the SRL report). It suggested that the sample be consumed by degradation. The expected product cyclopentadiene was observed at 220°C, which was 10°C below the corresponding data from poly(amic amide)/DNI-3A.

The DSC experiments were run for DNI-3A and PAA/DNI-3A under both ambient and high pressure (750 psi) environments. The DSC result for PAA/DNI-3A systems under ambient pressure condition is shown in Fig.5a. The region between 200°C to 350°C can be interpreted as a composite of an endotherm superposed on an exotherm. The endotherm started at about 200°C. The exotherm started at a higher temperature and showed a peak at about 280°C. At even higher temperature, the exothermic reaction overshadowed the endothermic reaction. The peak at 343°C was the tail section of the exotherm. This interpretation can be substantiated by studying the pressured DSC result shown in Fig.5b. The exotherm is due to the ring closure imidization reaction and the crosslinking reaction of the nadic end groups. The endotherm is from the evolution of cyclopentadiene. Under the pressurized condition, the evolution of cyclopentadiene was suppressed and the DSC

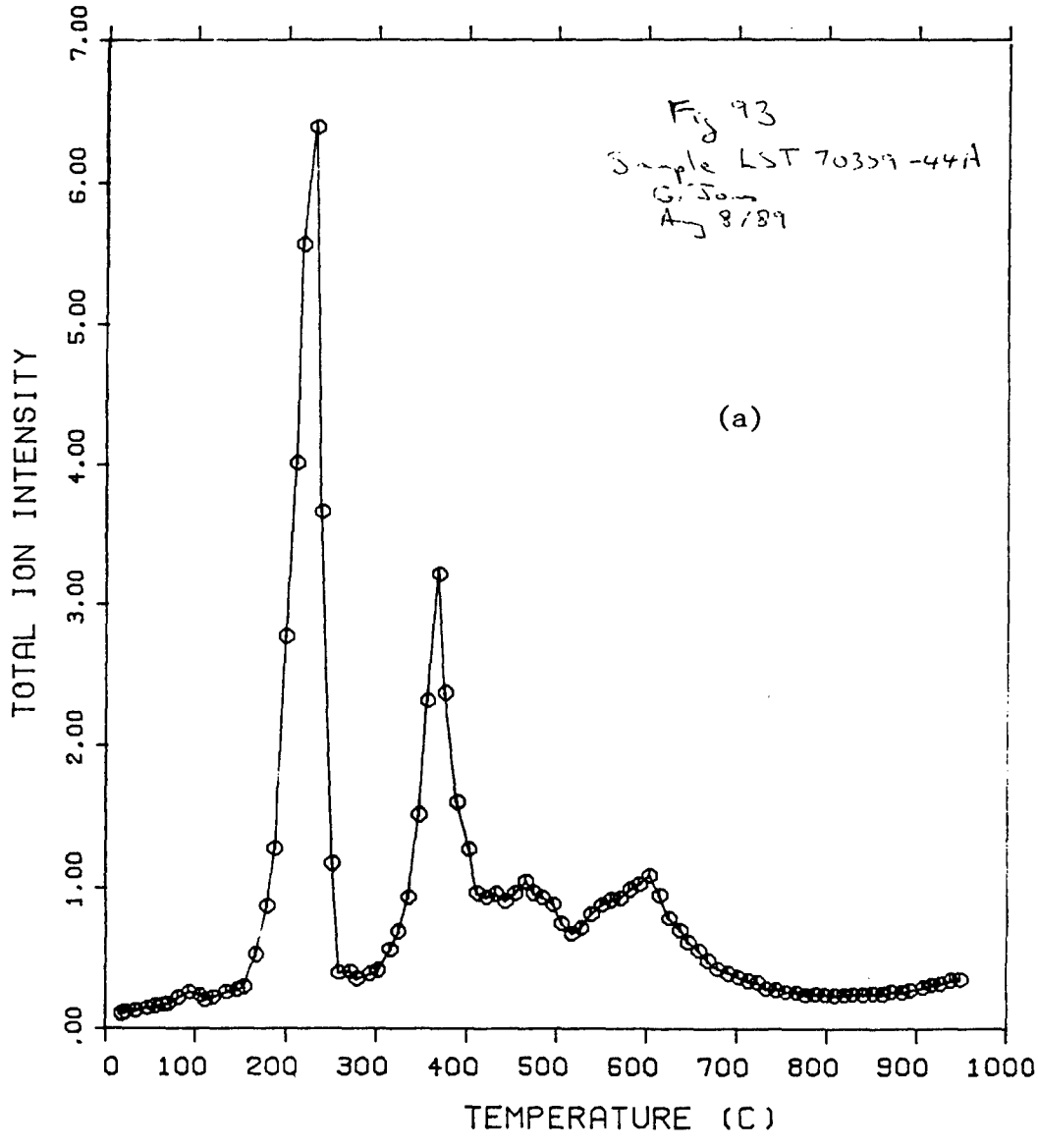


Fig.4. TGA/MS spectra for (a) PAA/DNI-3A, and (b) DNI-3A

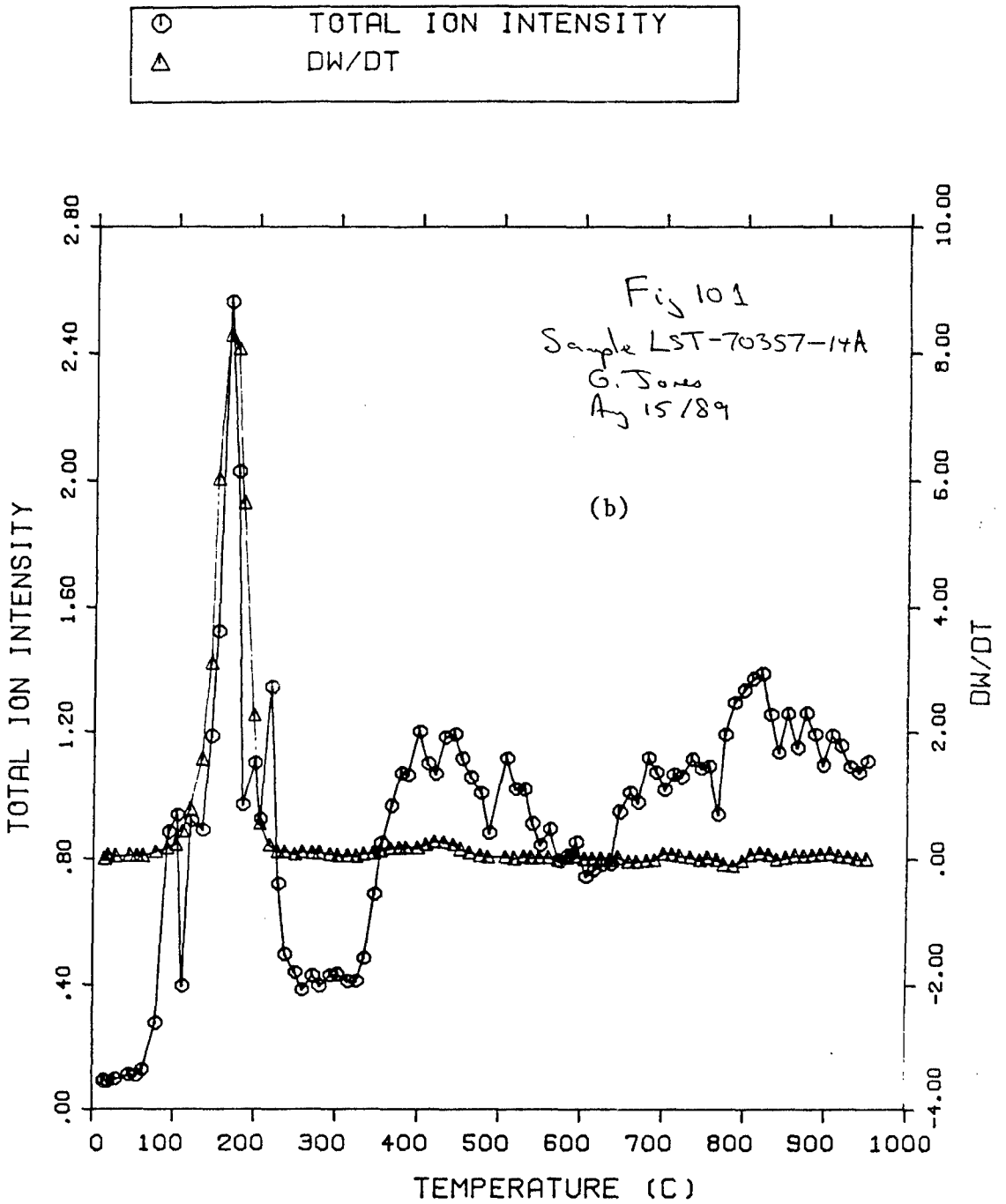


Fig.4. (continued)

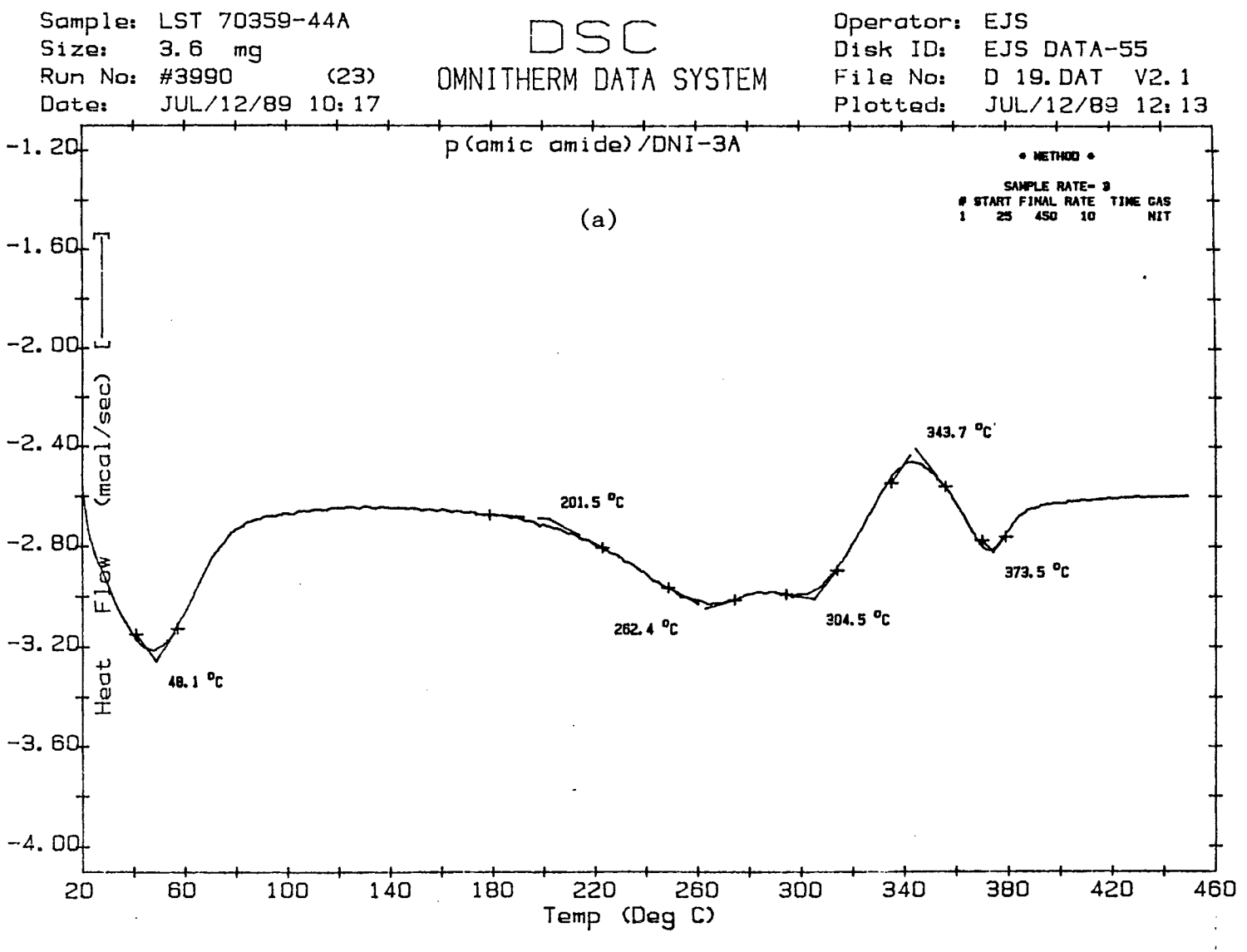


Fig.5. DSC thermogram for PAA/DNI-3A under (a) ambient, and(b) 750psi pressure, and for DNI-3A under (c) ambient, and (d) 750psi pressure

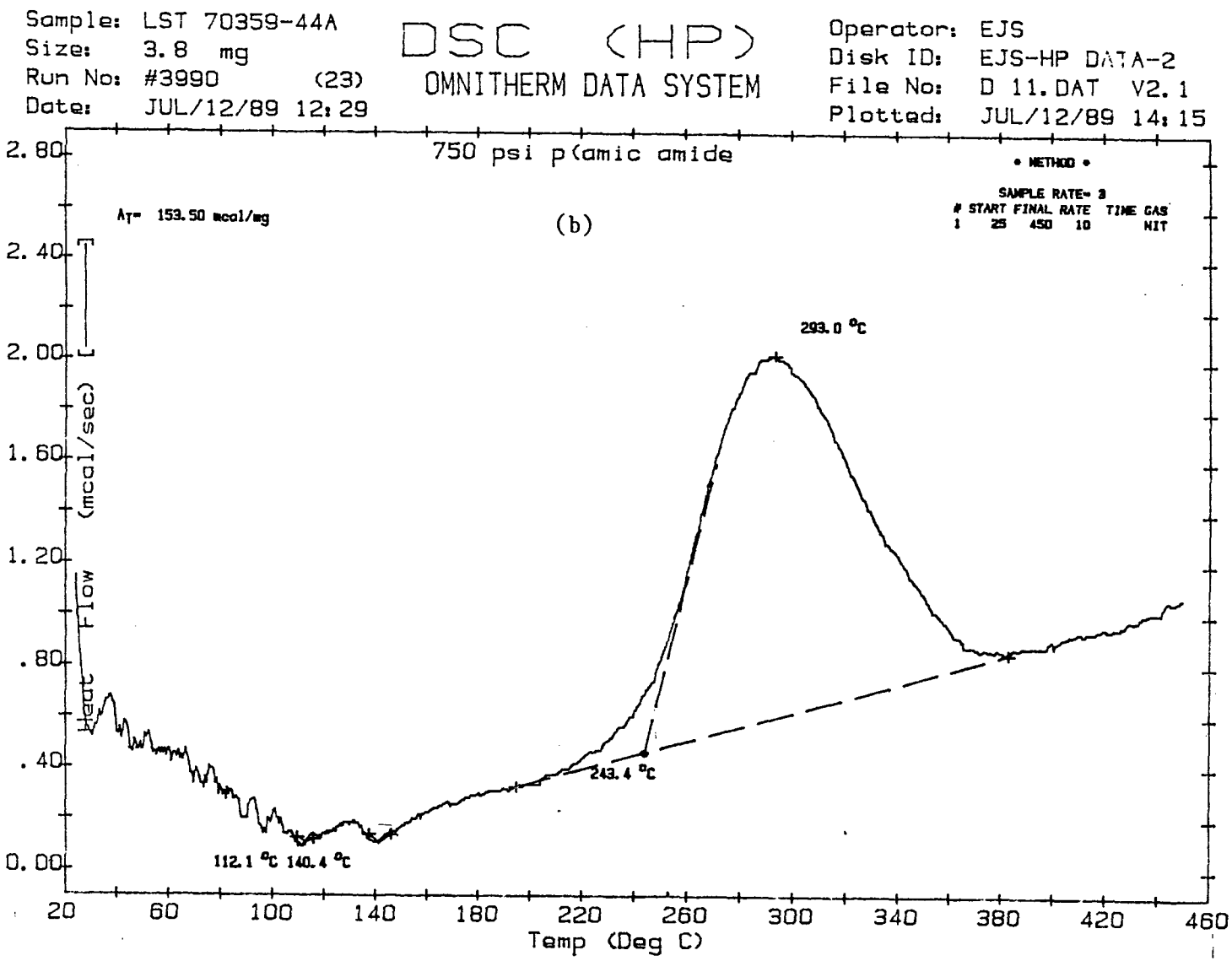


Fig.5. (continued)

showed only the exothermic component. The exotherm showed a well-behaved profile and peaked at ~290°C. The high temperature tail section of the exotherm corresponded nicely with the high temperature peak (343°C) shown in Fig.5a.

The DSC result of the model leaving group, DNI-3A, is shown in Figs.5c and 5d. The unpressurized DSC result in Fig.5c shows a melting endotherm at about 92°C. Another endotherm starts at about 200°C. This endotherm is due to the evaporation of the cyclopentadiene which is released from the decomposition of the nadic end group. The decomposed end groups can not crosslink at higher temperature. Thus no appreciable exotherm is shown in Fig.5c. The pressurized DSC in Fig.5d shows a similar melting endotherm at about 90°C. Evolution of cyclopentadiene is suppressed by the pressure. Two exotherms can be detected peaking at 272°C and 322°C respectively. Crosslinking reactions will occur at higher temperature if the cyclopentadiene evolution can be suppressed by external pressure.

4.2 FTIR Spectra and Subtraction Results

FTIR was used to study the imidization kinetics. In this study three different temperatures were chosen for the PAA/DNI-3A film reaction, namely, 240, 260 and 280°C. The typical FTIR results were shown in Figs.6a to 6c. The detail spectra for the polymers during the imidization were shown in Appendix C. The spectra changes were enhanced by subtracting the spectrum at t=0 from the spectrum collected at different times. The base line was offset by an arbitrary unit to display the negative side of the subtraction. The typical subtraction results were shown in Figs.6d and 6e. The details of the resultant charts from subtraction are shown in Appendix D.

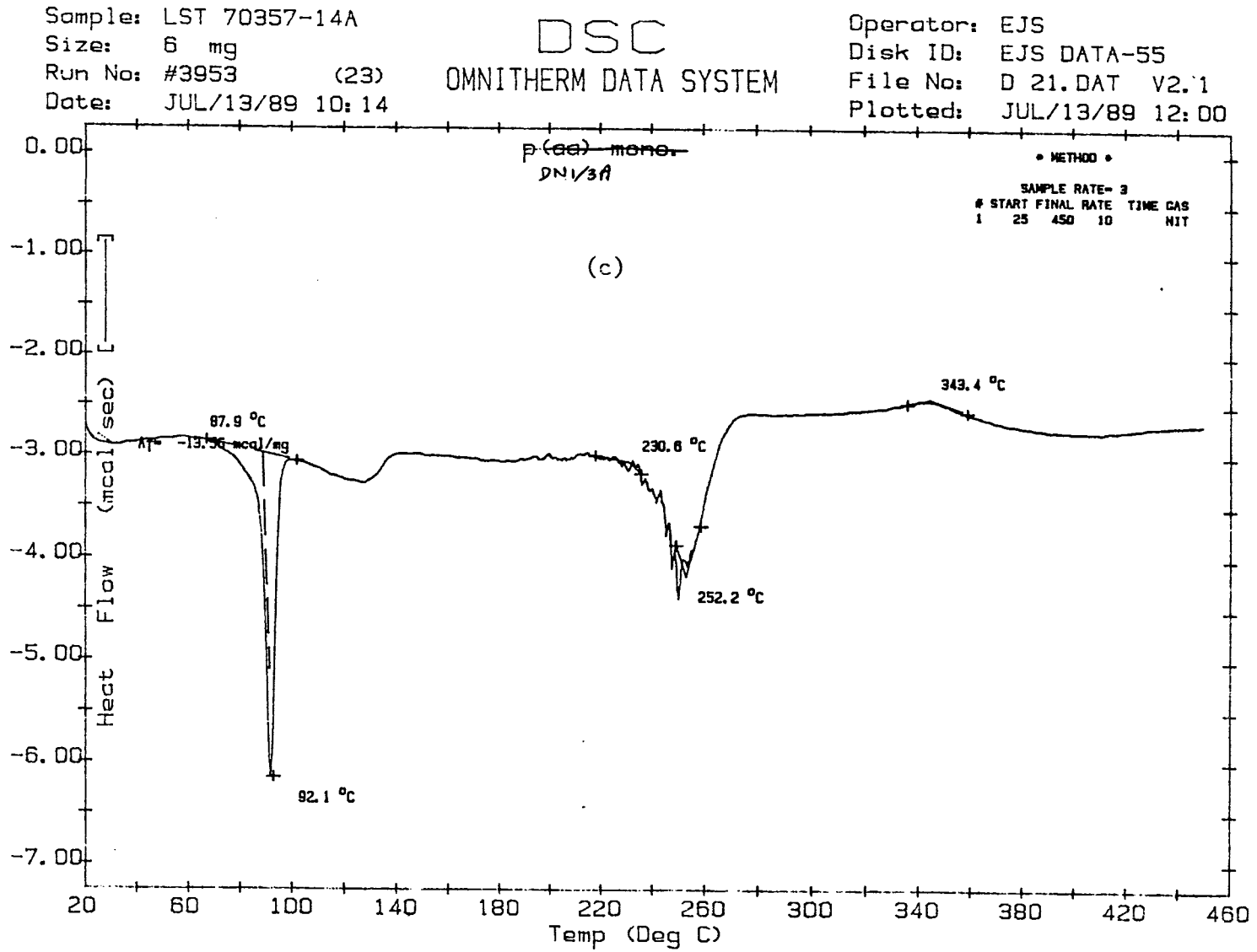


Fig.5. (continued)

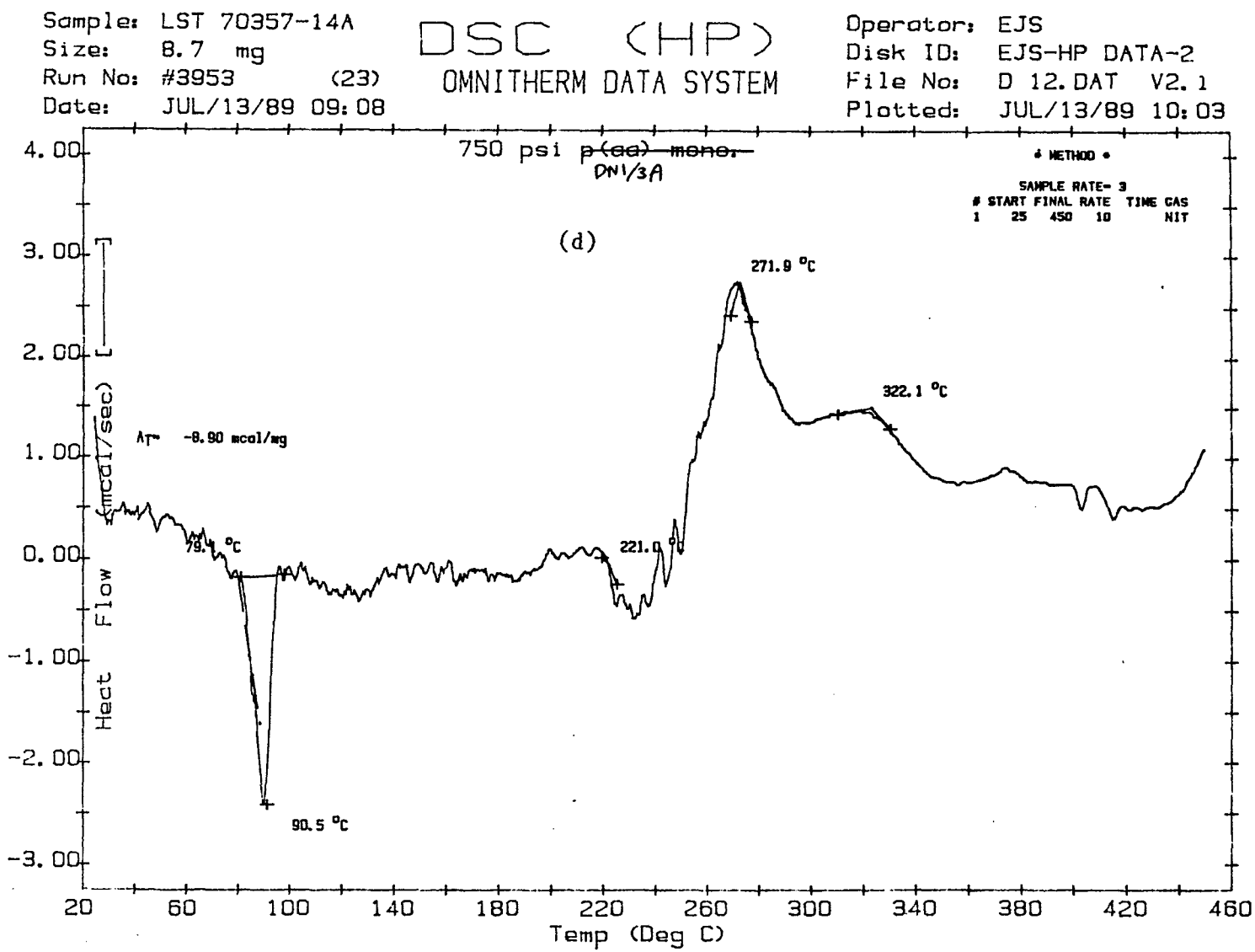


Fig.5. (continued)

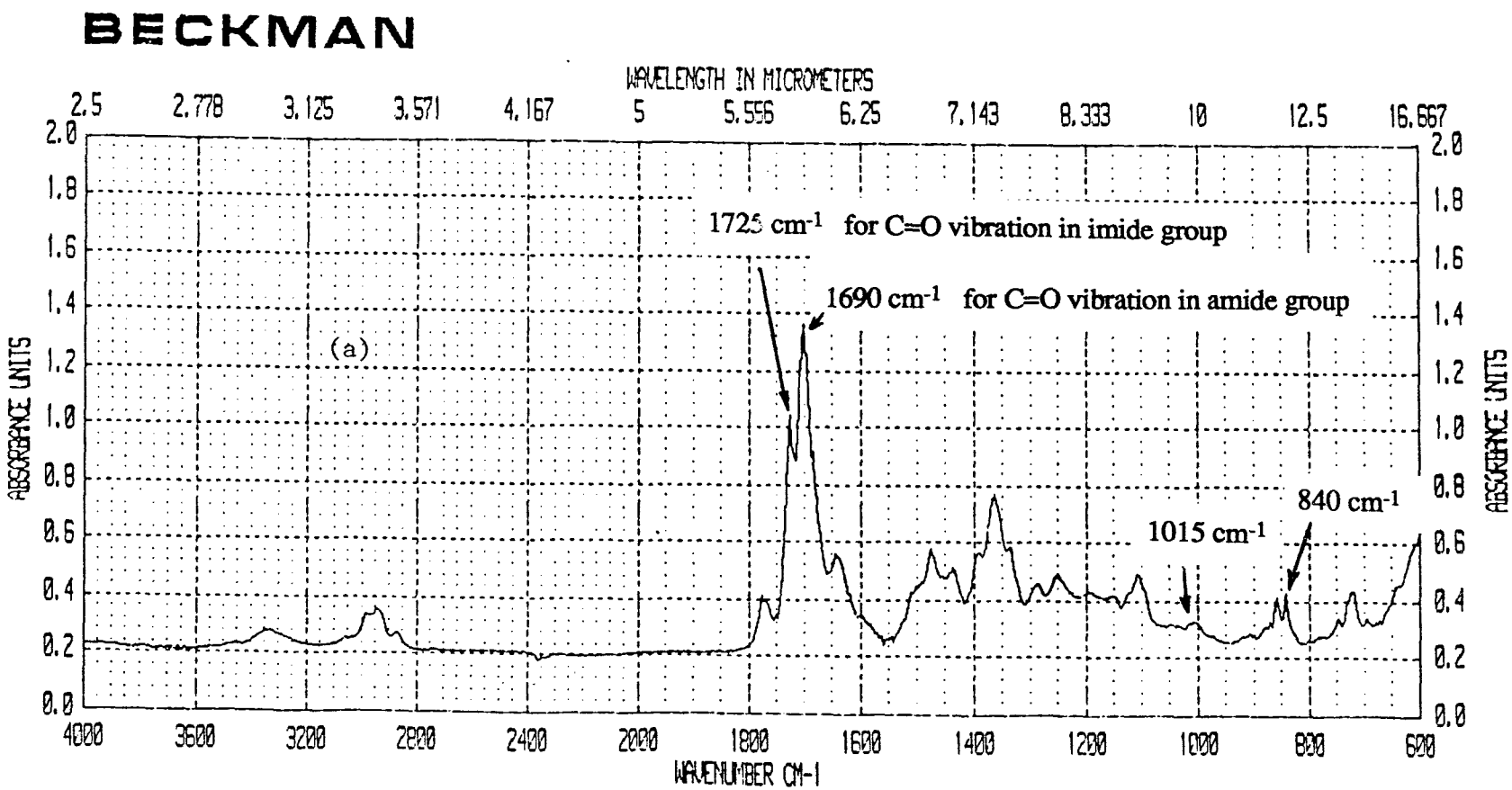


Fig.6. FTIR absorbance for PAA/DNI-3A at (a) 240°C, t =20 min, (b) 260°C, t=10 min, and (c) 280°C, t=10 min, respectively, and the subtraction results for (d) [A(t=5min)-A(0)], and (e) [A(t=180min)-A(0)] at 280°C

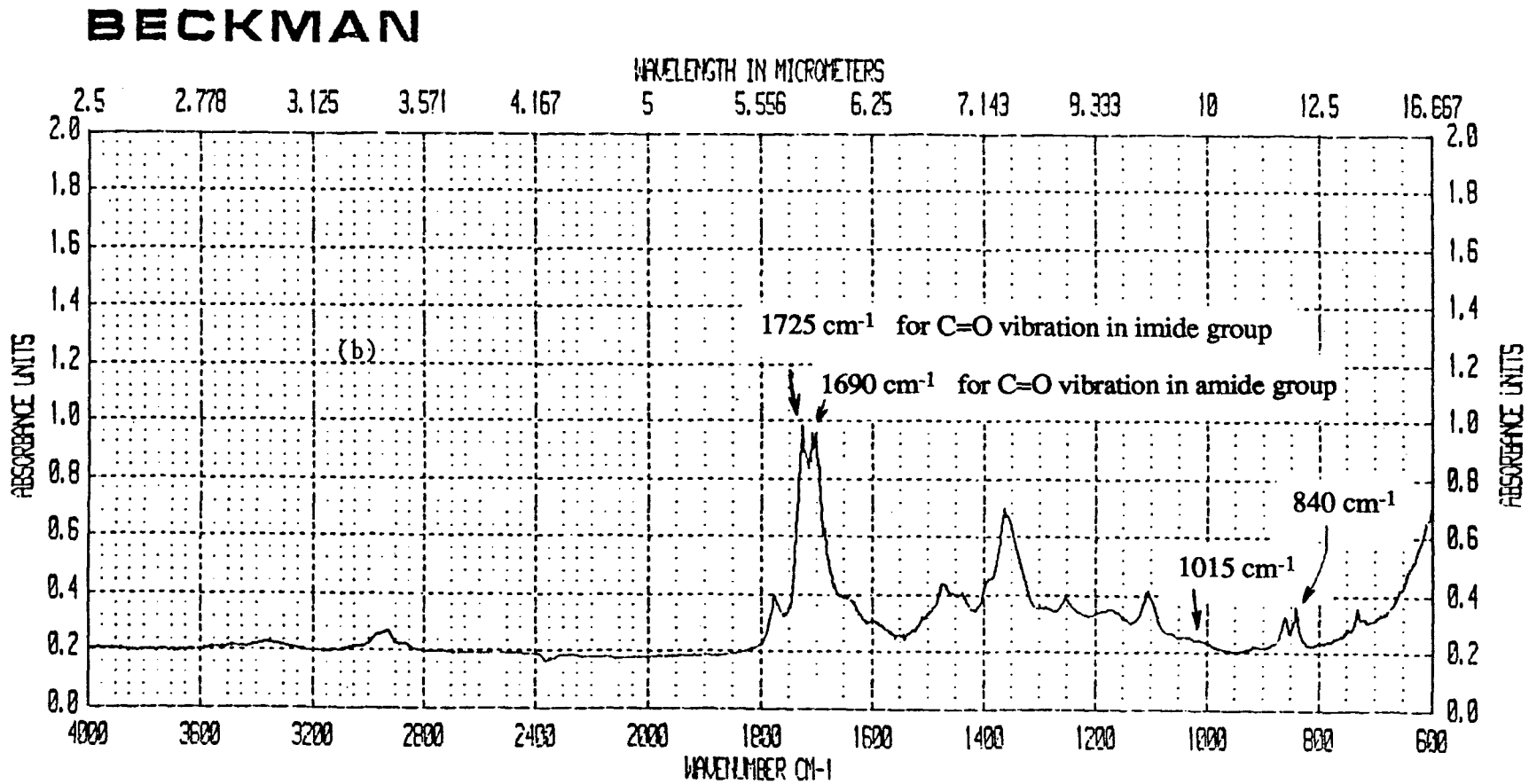


Fig.6. (continued)

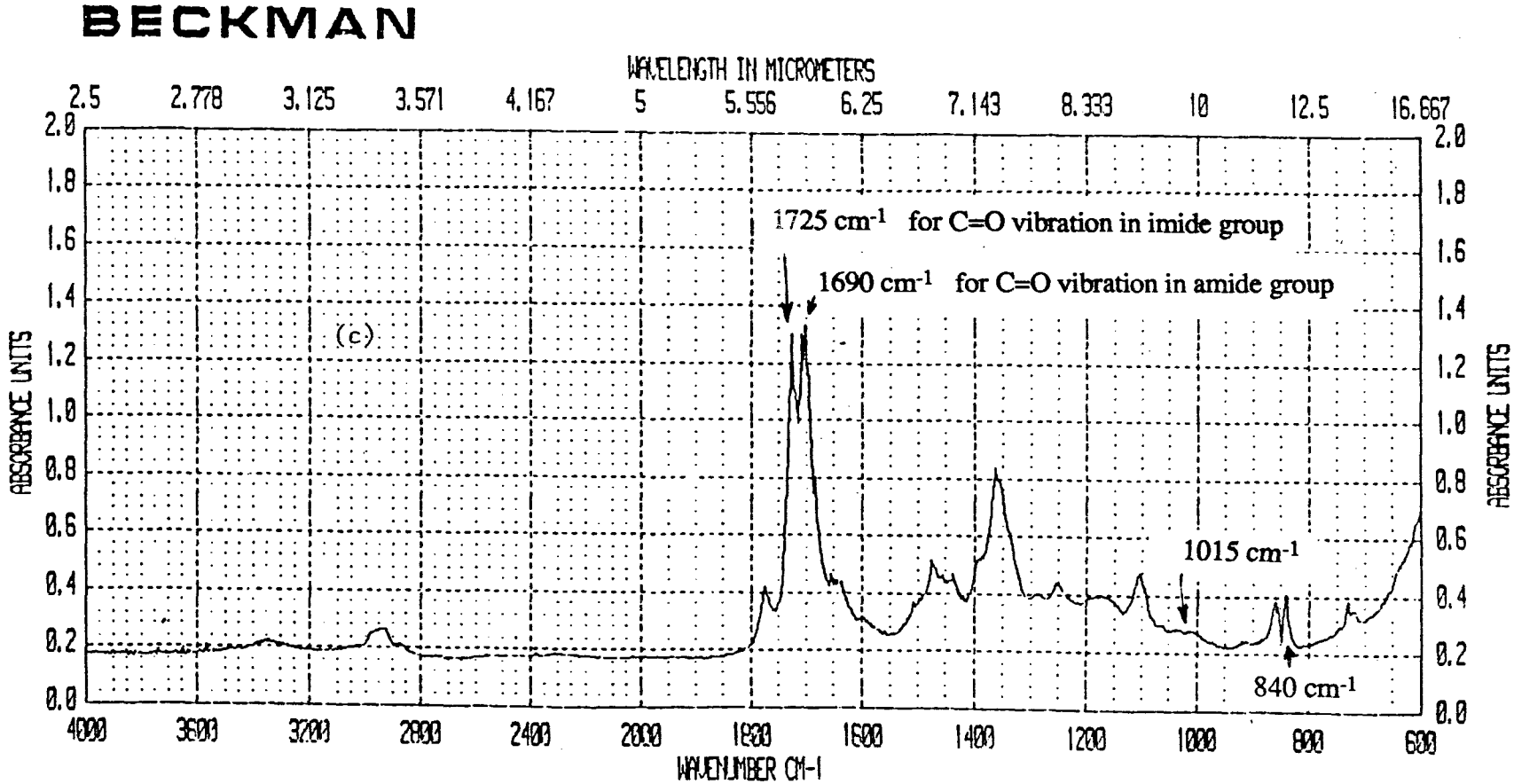


Fig.6. (continued)

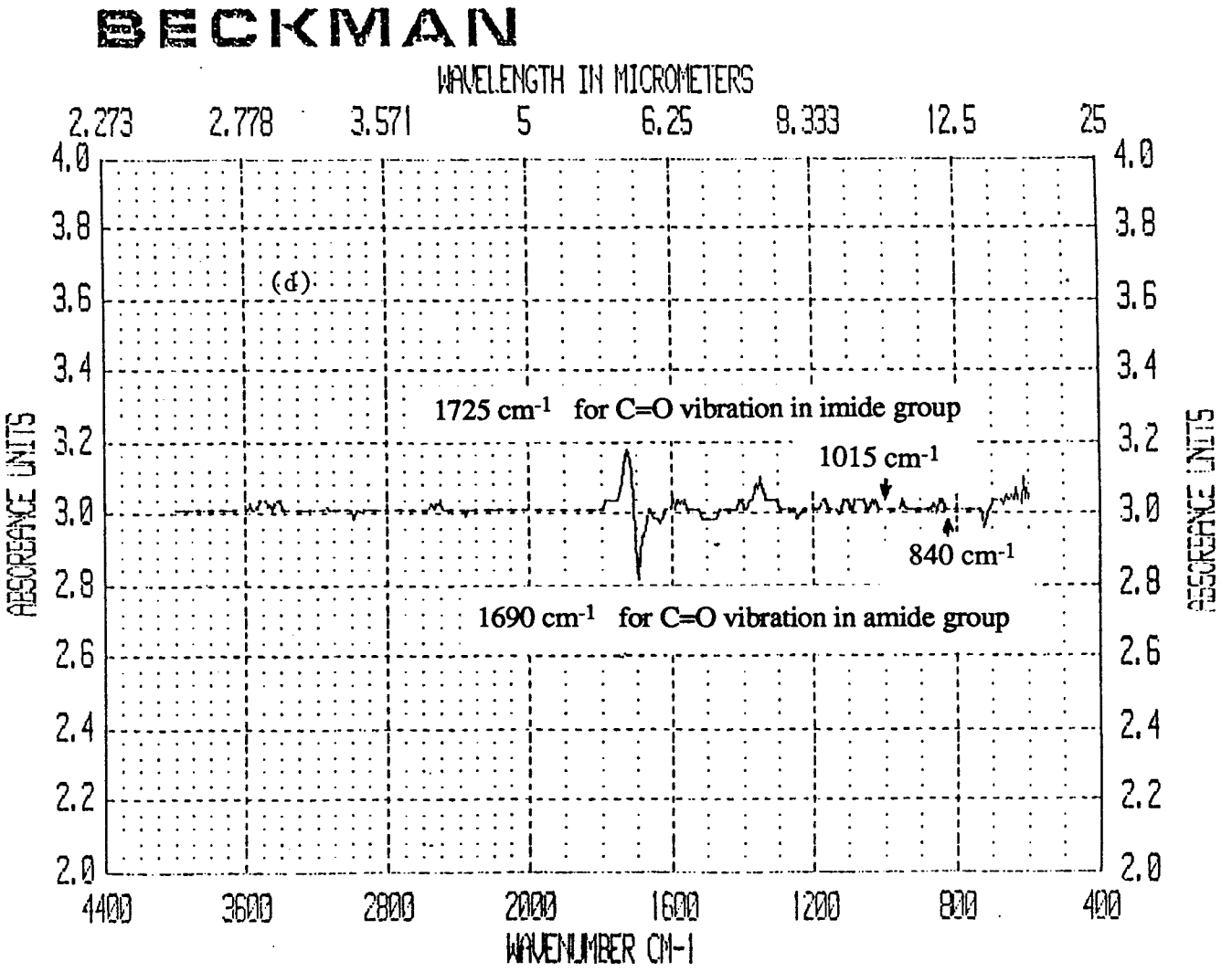


Fig.6. (continued)

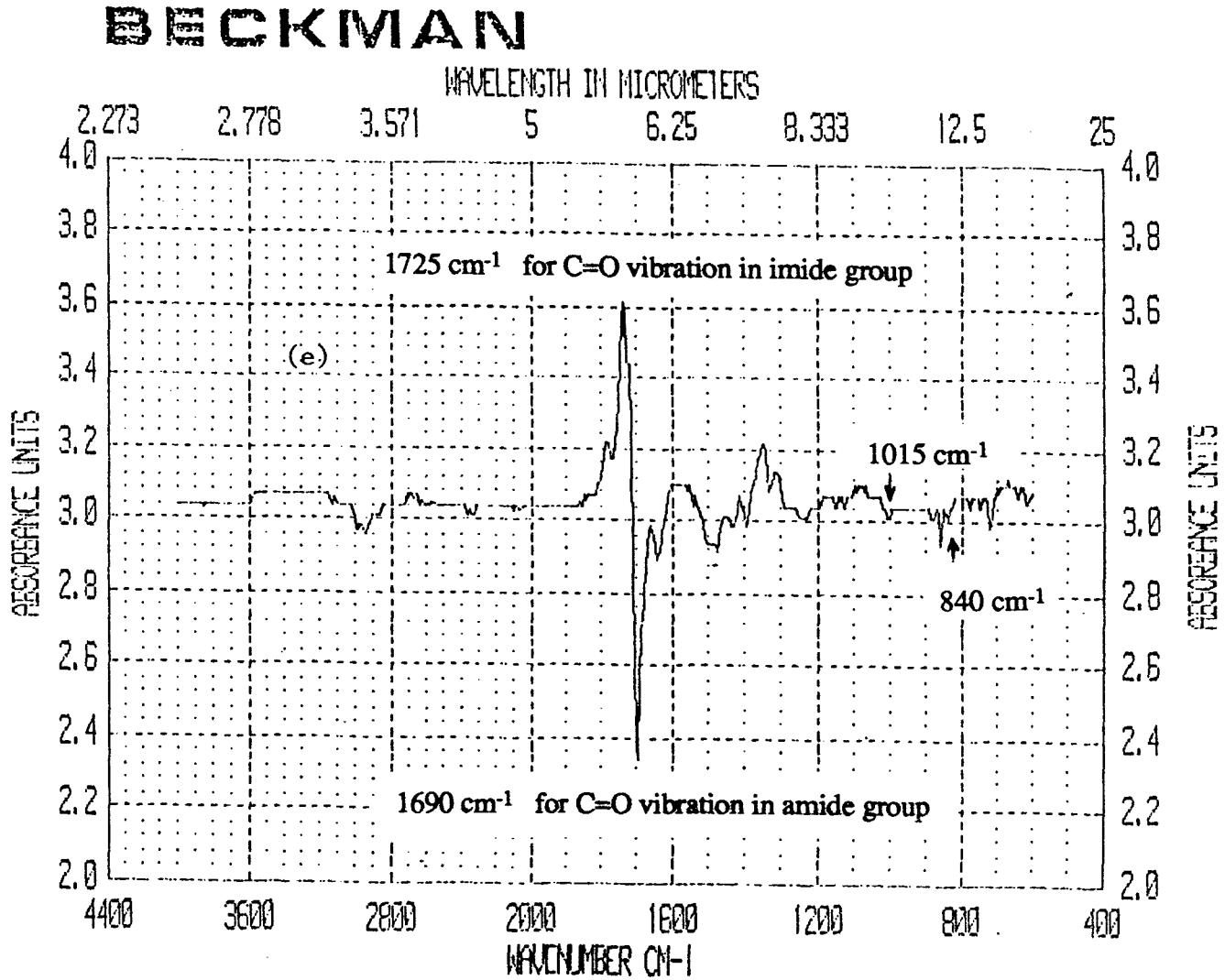


Fig.6. (continued)

In comparing the FTIR spectra from different samples, one should notice the thickness effect since different thickness cause different amount of peak intensity. From the literature the internal reference is chosen at 840 cm^{-1} (C-H out-of-plane bending from p-substituted benzene) [22] or 1015 cm^{-1} (C-H in-plane bending from p-substituted benzene) peak [23,24]. In this report the 1015 cm^{-1} was chosen. (Indeed, both bands do not change much). With this reference peak the relative thickness was calibrated and the correct peak intensity was obtained.

4.3 FTIR Absorption Bands for PAA/DNI-3A and Polyimide

The characteristic bands of amide or imide is from its carbonyl vibration. The band at 1690 cm^{-1} was assigned as the stretching vibration of the secondary amide. The 1640 cm^{-1} peak is assigned to the tertiary amide. For imide, the peaks assigned are 1775 (1780), 1725, 1350 (1370), and 735 (720) cm^{-1} [9,12,13,17,18,22-29] (see Table 2.) The increasing or decreasing of the aforementioned peaks during imidization was observed. But not every peaks can be quantitatively characterized due to the noise in the data. The most significant changes of the peaks are those of 1690 and 1725 cm^{-1}. The former one is an amide peak along the unreacted backbone while the latter one is associated with the resultant imide [30]

The comparison of the normalized data from increasing intensity of 1725 cm^{-1} peak with that from the decreasing intensity of 1690 cm-1 peak at 280°C is shown in Fig.7a. The good agreement between the increase of 1725 cm^{-1} peak and the decrease of 1690 cm^{-1} peak at 280°C suggested that there is no intermediate formed during the amide-imide conversion. Similar plots for 260C and 240C experiments are shown in Figs. 7b and 7c. The agreement between these two peaks were not that good at 240°C due to the noise effect on the relative small value of the denominator $\Delta A(0,\tau)$. But they are still in the same range

Table 2. The assigned imide peaks in the literature

Ref.No.	Absorption Peaks (cm^{-1})
9.	720*,1725, 1780 (* used for kinetics, ref. 995 for Aromatic ring vibration)
12.	725
13.	1380*, 1780 (recommended)
17.	1780
18.	725 (ref 1480 for aromatic structure)
22.	720, 1370, 1720, 1780 (ref. 820 for C-H)
23.	1720,1780 (ref.1012)
24.	725, 1380 (ref 1015 for aromatic ring vibr.)
25.	1380, 1780
26.	1380,1720,1780
27.	730, 1370*, 1780 (* recommended)
28.	700, 1776
29.	725, 1778 (ref 1480 for aromatic structure)

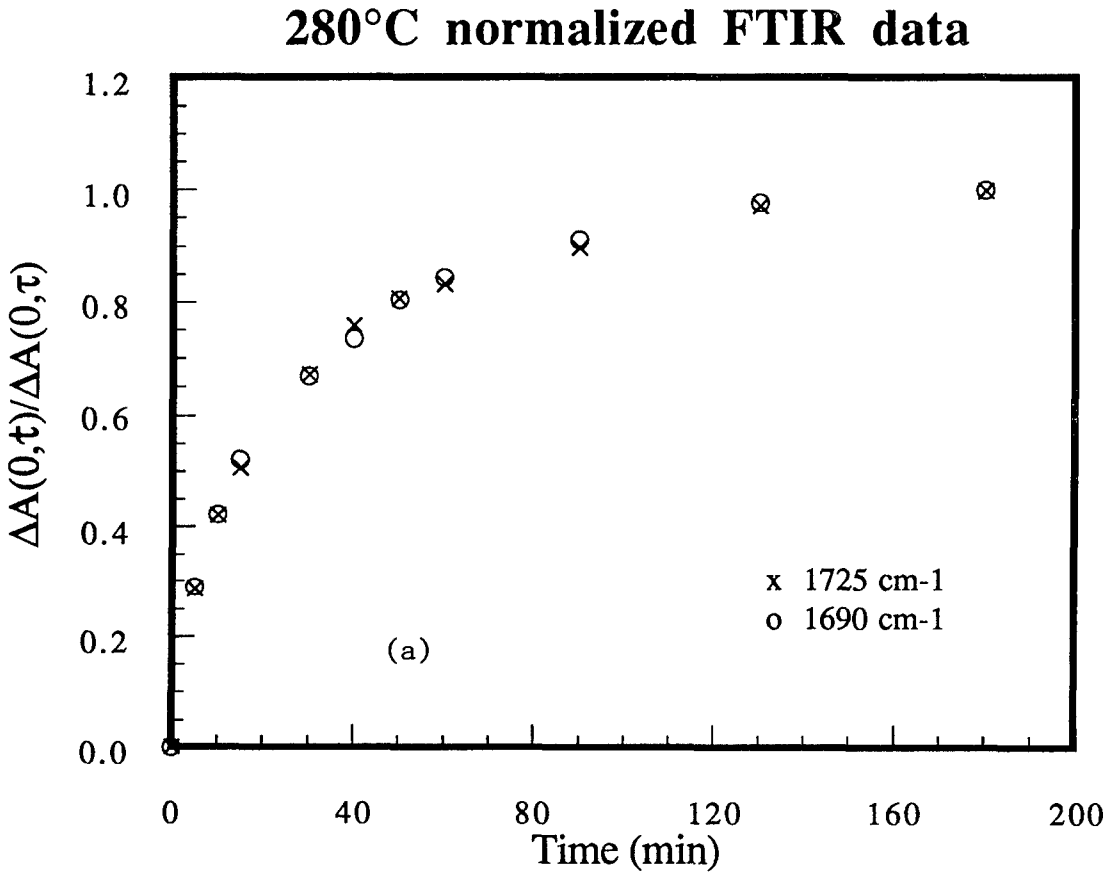


Fig.7. Normalized absorption at increasing peak 1725 cm^{-1} and decreasing peak 1690 cm^{-1} for PAA/DNI-3A during imidization at (a) 280°C, (b) 260°C, and (c) 240°C

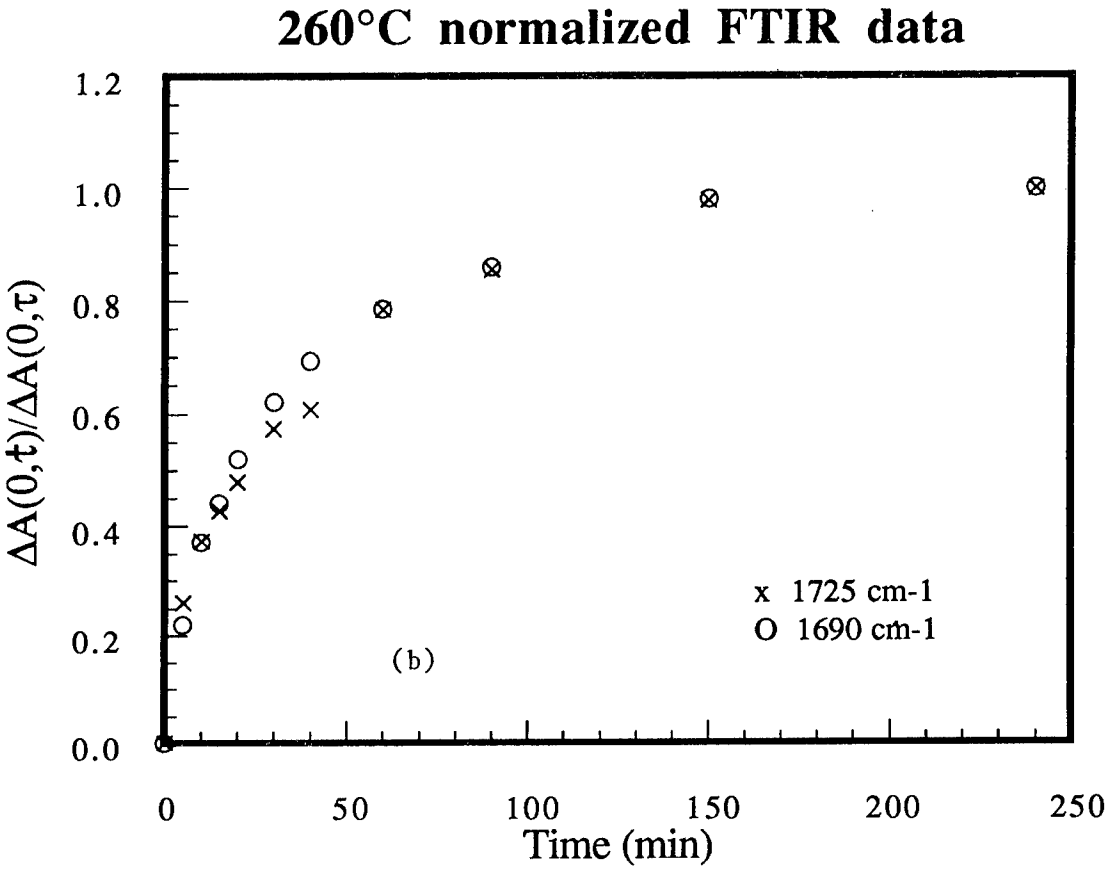


Fig.7. (continued)

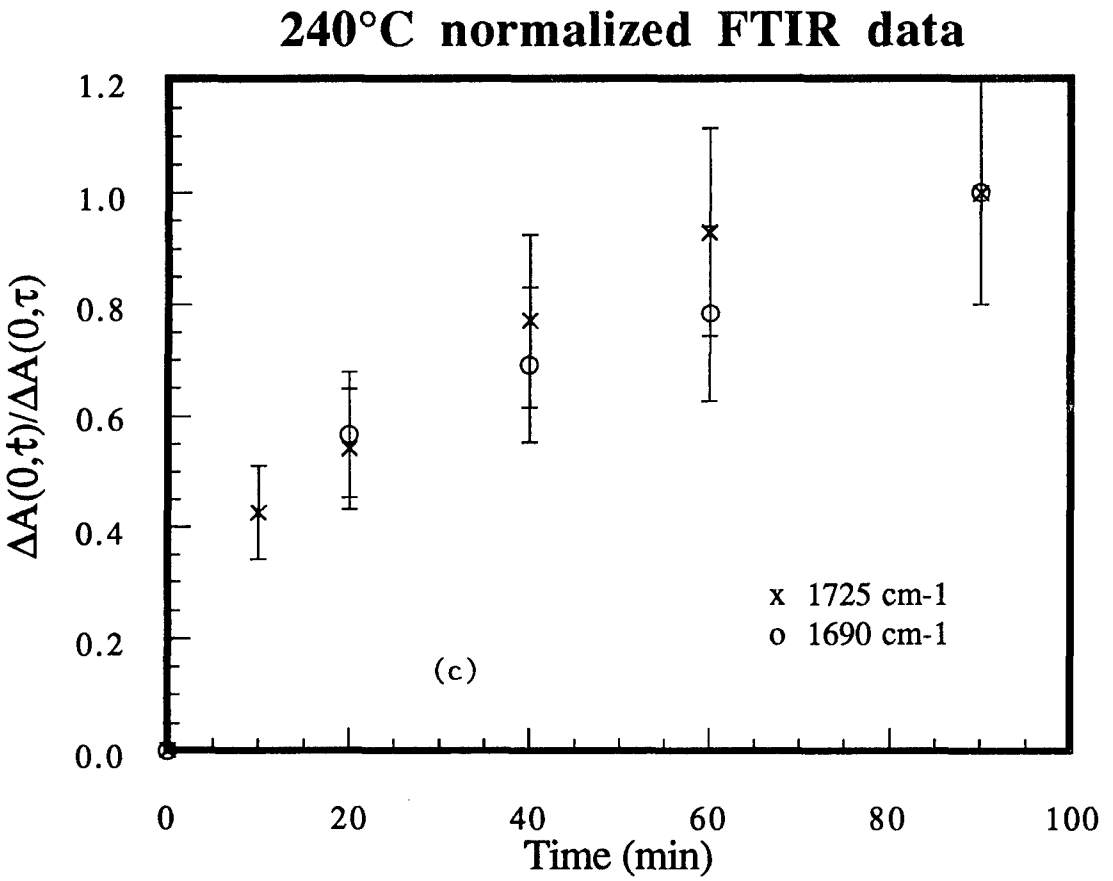


Fig.7. (continued)

after the error from noise (±20%) is taken into account. It is worth noting that the imidization at these two temperatures for 4 hours is not complete.

4.4. $([C]_t-[C]_\tau)/([C]_0-[C]_\tau)$ Concentration Ratio Analysis and Kinetic Parameters

As explained in Section 3.3, the kinetic data can be characterized by equations (6) or (7). At 280°C let τ =180 minutes. It was noticed that the imidization is very close to completion at 280°C for 180 minutes (this point will be verified in Section 4.5), i.e., A(180 min)~A(∞) at 280°C. From Beer's Law, the path-independent characteristic absorbance of any moieties for different specimen at any temperature T can be represented by the following equation:

$$\Delta A(0,\infty)_{280°C}/b_{280°C} = \Delta A(0,\infty)_T/b_T$$

or

$$\Delta A(0,\infty)_T = \Delta A(0,\infty)_{280°C} * b_T/b_{280°C} \qquad (12)$$

where $\Delta A(0,\infty)_{280°C}$ is A(0)-A(∞) at 280°C. The path (or thickness) ratio, $b_T/b_{280°C}$, can be calibrated by the absorbance of the internal reference peak at 1015 cm^{-1}. [Note: This peak was not very obvious in the absorption spectrum, but can be readily detected in the computer "pick-peak" option.] In equation (12) the notation ∞ can be interchanged with time τ without losing any generality. This equation provides an easy way to calculate the corresponding value of $\Delta A(0,\infty)_T$ for different specimen at temperature T. The function $\ln\{([C]_t-[C]_\tau)/([C]_0-[C]_\tau)\}$ (or $\ln\{[A(t)-A(\tau)]/\Delta A(0,\infty)_T$ with the understanding that $\Delta A(0,\infty)_T$ comes from equation (12)) were plotted verse time. The results were shown in Figs.8a-8c for 1725 cm^{-1} and Figs.8d-8f for 1690 cm^{-1} at different temperatures. From the plots it is observed that there are two first order stages during the whole reaction process. The slopes of the curves, which were the (-k) values at that temperature, were calculated by the least square method. These k values are listed in Table 3.

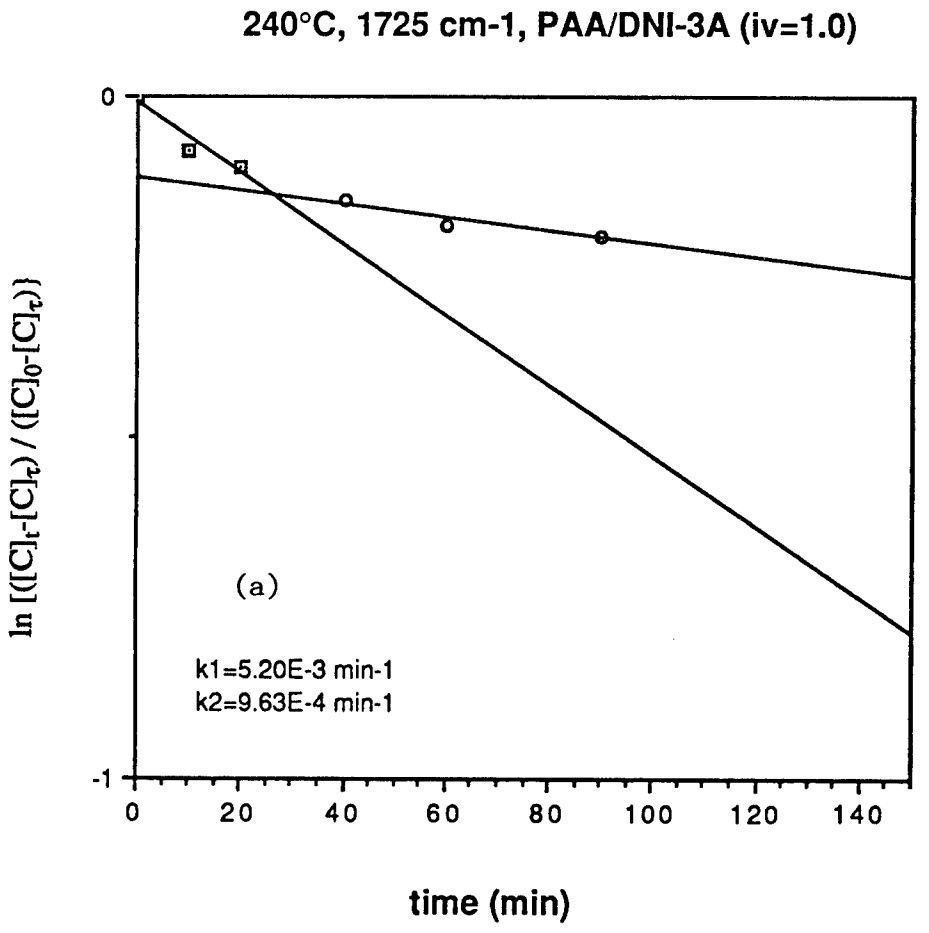


Fig.8. ln $([C]_t-[C]_\tau)/([C]_0-[C]_\tau)$ versus time for PAA/DNI-3A at 1725 cm^{-1} at (a) 240°C, (b) 260°C, and (c) 280°C, and at 1690 cm^{-1} at (d) 240°C, (e) 260°C, and (f) 280°C

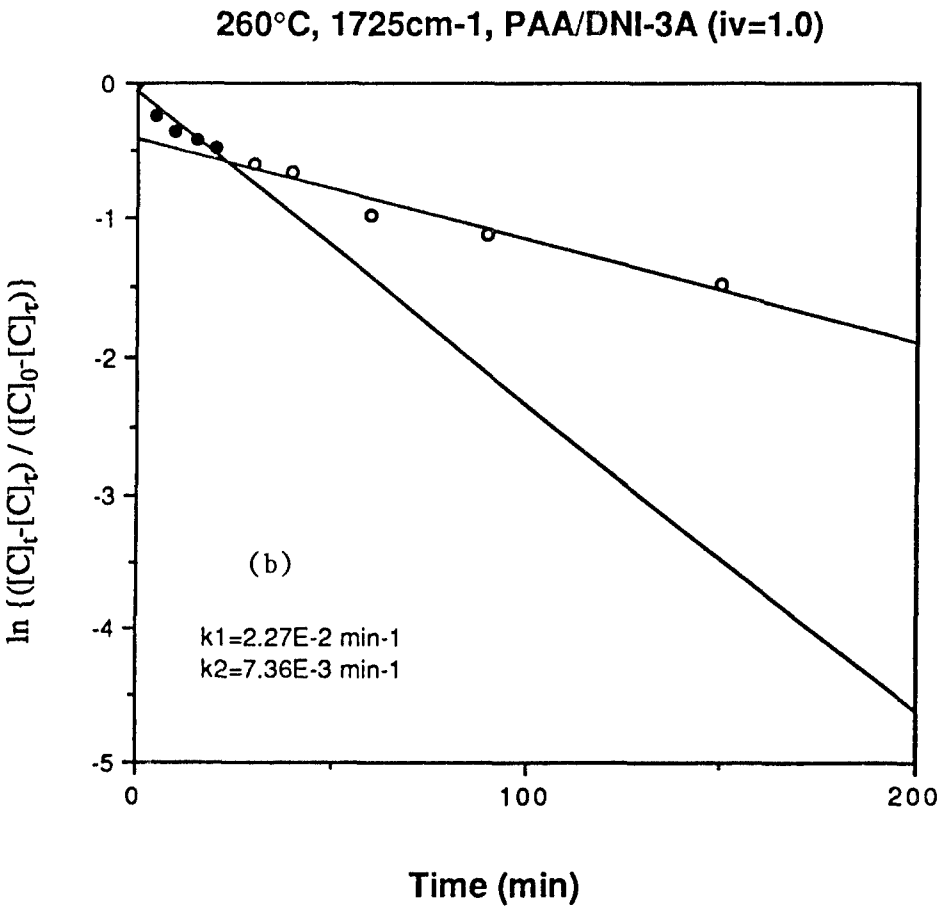


Fig.8. (continued)

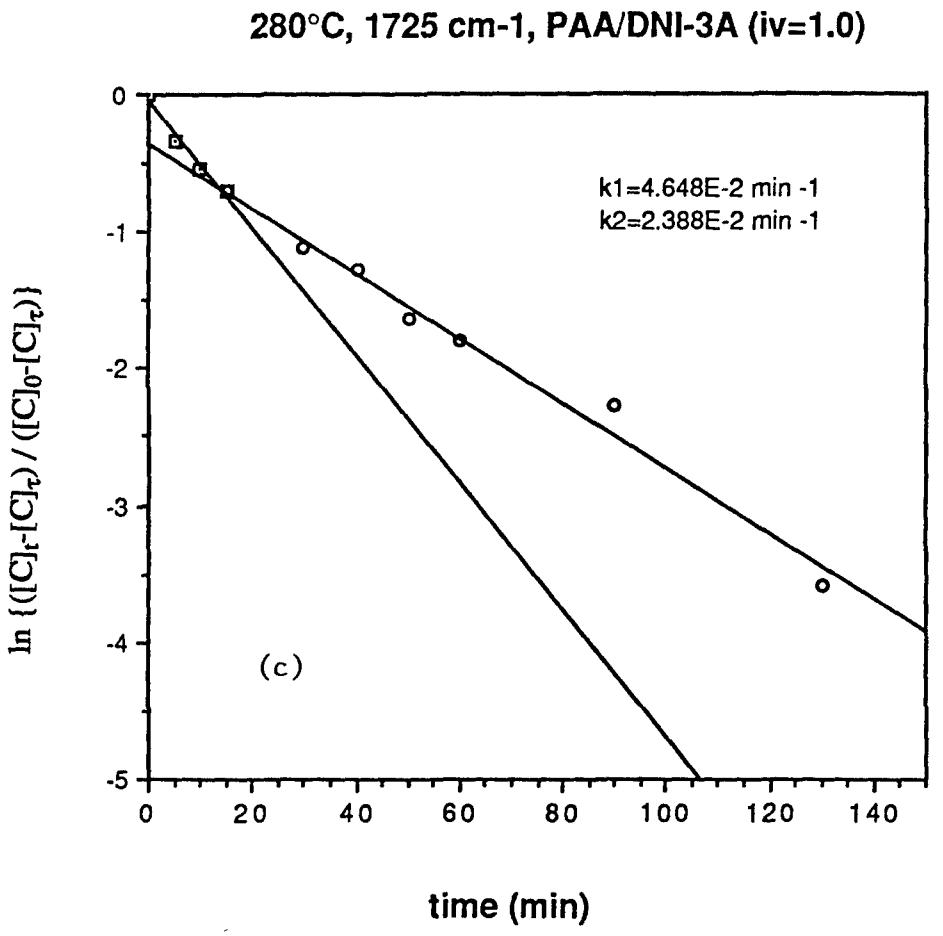


Fig.8. (continued)

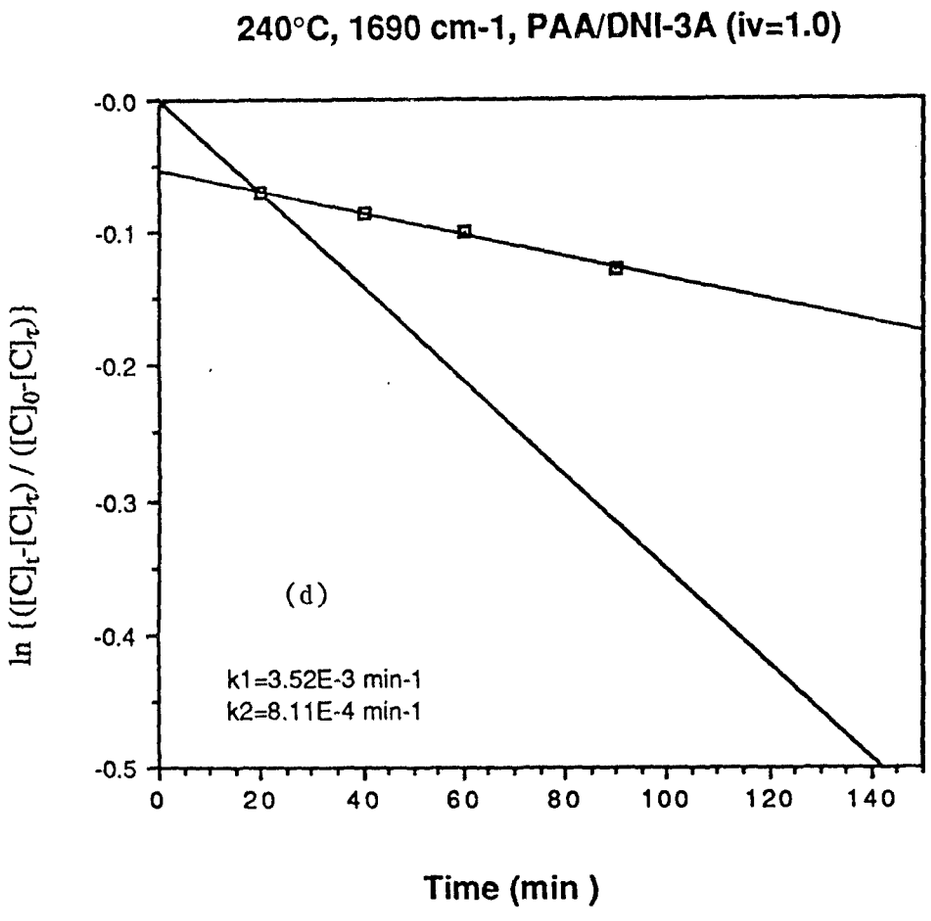


Fig.8. (continued)

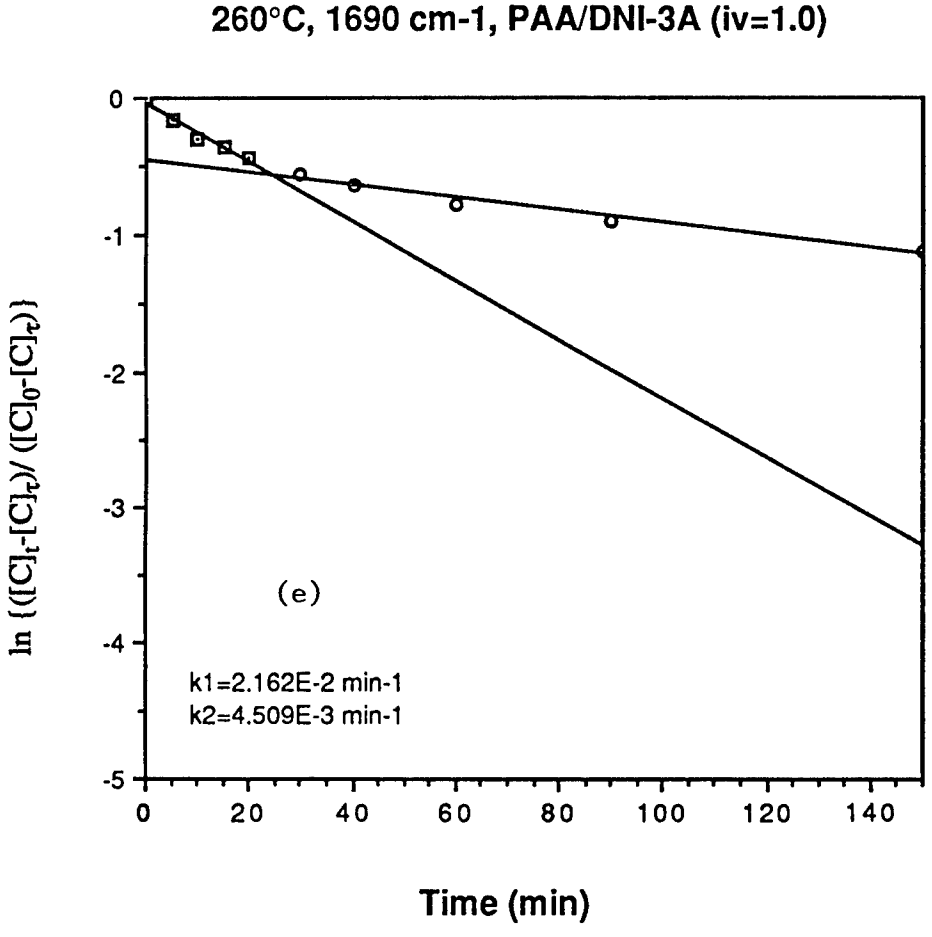


Fig.8. (continued)

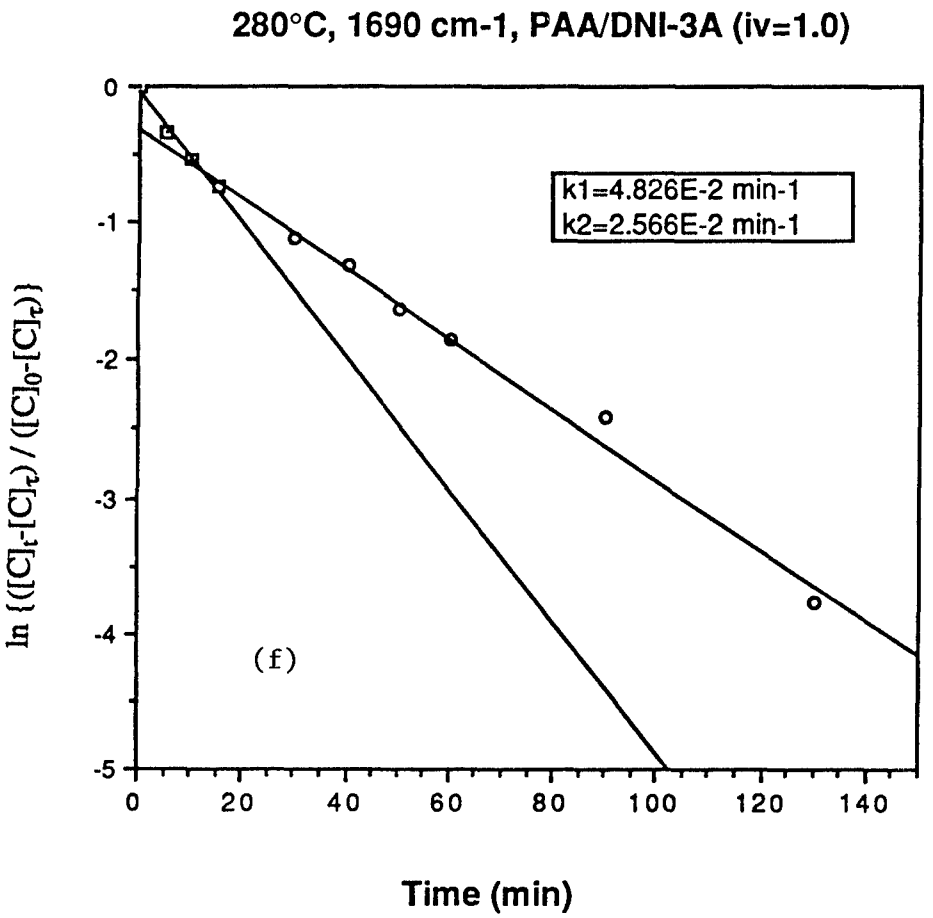


Fig.8. (continued)

Table 3. The kinetic parameters of imidization from

$([C]_t-[C]_\tau)/([C]_0-[C]_\tau)$ data

(a) at 1725 cm^{-1}

k_1 (min^{-1})			k_2(min^{-1})		
280°C	260°C	240°C	280°C	260°C	240°C
4.684E-2	2.27E-2	5.20E-3	2.388E-2	7.36E-3	9.63E-4

(b) at 1690 cm^{-1}

k_1 (min^{-1})			k_2(min^{-1})		
280°C	260°C	240°C	280°C	260°C	240°C
4.826E-2	2.162E-2	3.52E-3	2.566E-2	4.51E-3	8.11E-4

4.5 ΔA Absorbance Difference Analysis and Kinetic Parameters

The above analysis based on concentration ratio data, $([C]_t-[C]_\tau)/([C]_0-[C]_\tau)$, is subject to error in calculating the kinetic data k values because of the possible non-zero value of $[C]_\tau$ as mentioned in Section 3.3. The data were following the absorbance difference, ΔA, analysis mentioned in Section 3.4. Since the initial data set was not in equally spaced time basis, the interpolation of the data is required. There are two ways to interpolate the data, direct and indirect. The direct interpolation simply was done from the original data set while the indirect way would be done after some massage of the original data. It is noted that the raw data shown in Figs.8a-f are not smoothly distributed. When the equally spaced time data were directly interpolated from these scattered data, the logarithm of the difference, $\ln[\Delta A(t_1,t_2)]$, for each pair of data will become very scattering. Significant error will be generated by this way of data treatment. It is this sensitivity that the indirect way, the least-square-fitted curves in Figs.8a-f, were used to interpolate the equally spaced time data for the $\Delta A/[A(\tau)-A(0)]$ readings. The ΔA data were then obtained by multiplying $[A(\tau)-A(0)]$ with the interpolation values. After this conversion the ΔA values really represent the true difference between any two different times no matter how the $([C]_t-[C]_\tau)/([C]_0-[C]_\tau)$ data were distorted from the true first-order one by the non-zero $[C]_t$ value since the $([C]_0-[C]_\tau)$ values do not play any role in the ΔA terms. In principle, this is just the interpolation of $[C]_t$ or A(c,t) value, nothing to do with $[C]_\tau$ value. Recall that, from Section 3.4,

$$\begin{aligned} \ln \Delta A(t_1, t_2) &= \ln k' - kt_1 + \ln\left\{1 - e^{-k(t_1 - t_2)}\right\} \\ &= k'' - kt_1 \end{aligned} \qquad (11)$$

The $\Delta t=t_1-t_2=5$ minute in the fast reaction period and $\Delta t=t_1-t_2=10$ minutes in the slow reaction period were then taken for ΔA readings. The results of [ln ΔA] verse t_1, based on

equation (11), were plotted and shown in Figs.9a-9c for 1725 cm^{-1} and Figs.9d-9f for 1690 cm^{-1} band. From each curves the slopes, i.e., the (-k) values, was computed by the least square method. The resultant k values are listed in Table 4.

From this Table it is clear that the corresponding k values derived from the concentration ratio, $([C]_t-[C]_\tau)/([C]_0-[C]_\tau)$, method and from fixed-time-interval data, ΔA, method are very close (within 2%). This implies that the τ (=180 min) ~ ∞ assumption is reasonable and that $[C]_\tau$ is indeed close to zero. Besides, by using the k values obtained from 280°C to back calculate the degree of conversion, $[C]_{\tau=180\ min}$ is only 1% of $[C]_0$. (Please note that this value is calculated from the 1725 cm^{-1} data. If the calculation is based on the 1690 cm^{-1} data, $[C]_{\tau=180\ min}$ is about 0.8% of $[C]_0$. In doing such calculation, the transition from k_1 to k_2 is set at time equal to 12 minutes as shown in Figs. 8 and 13.) Using the 1725 cm^{-1} data and the same calculation techniques, the corresponding time for the residue concentration, $[C]_t$, to reach 1% of $[C]_0$ is about 20 hours at 260°C and 80 hours at 240°C, respectively.

From the k values at different temperatures the Arrhenius plot can be employed to compute the activation energy and pre-exponent constant. Figs.10a and 10b and Table 4 show the results. It is noticed from the results that the activation energy is about 34±3 Kcal/mole for the fast reaction and 48±2 Kcal/mole for the slow reaction. Compared to the data from literature, the two values of activation energy are much higher, and the overall reaction constant, k, at the same temperature are quite different. However, the literature data are mostly the ring closure of amic ester while the reaction being studied in this report was amic amide.

A comparison of the k values for slow reactions between the current PAA/DNI-3A system and the PMR-15 system is given in Fig.11. Although the fast reaction constants were not

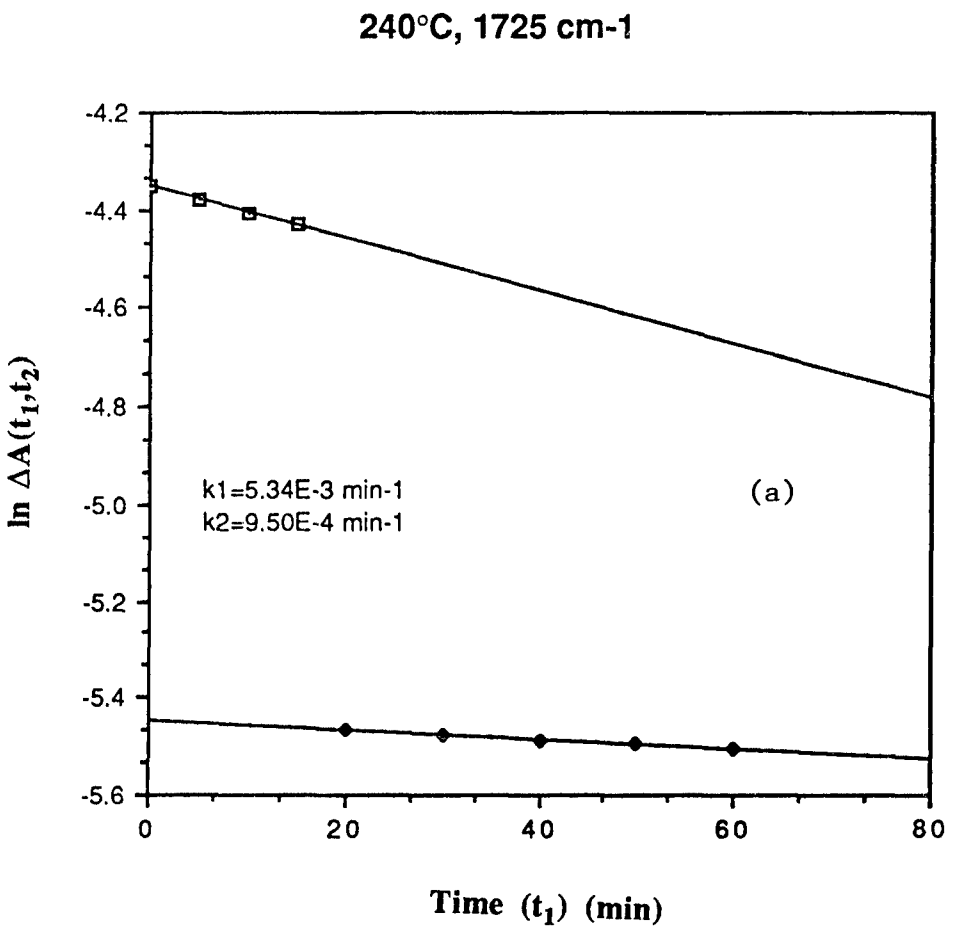


Fig.9. ln ΔA versus time for PAA/DNI-3A at 1725 cm^{-1} at (a) 240°C, (b) 260°C, and (c) 280°C, and at 1690 cm^{-1} at (d)240°C, (e) 260°C, and (f) 280°C

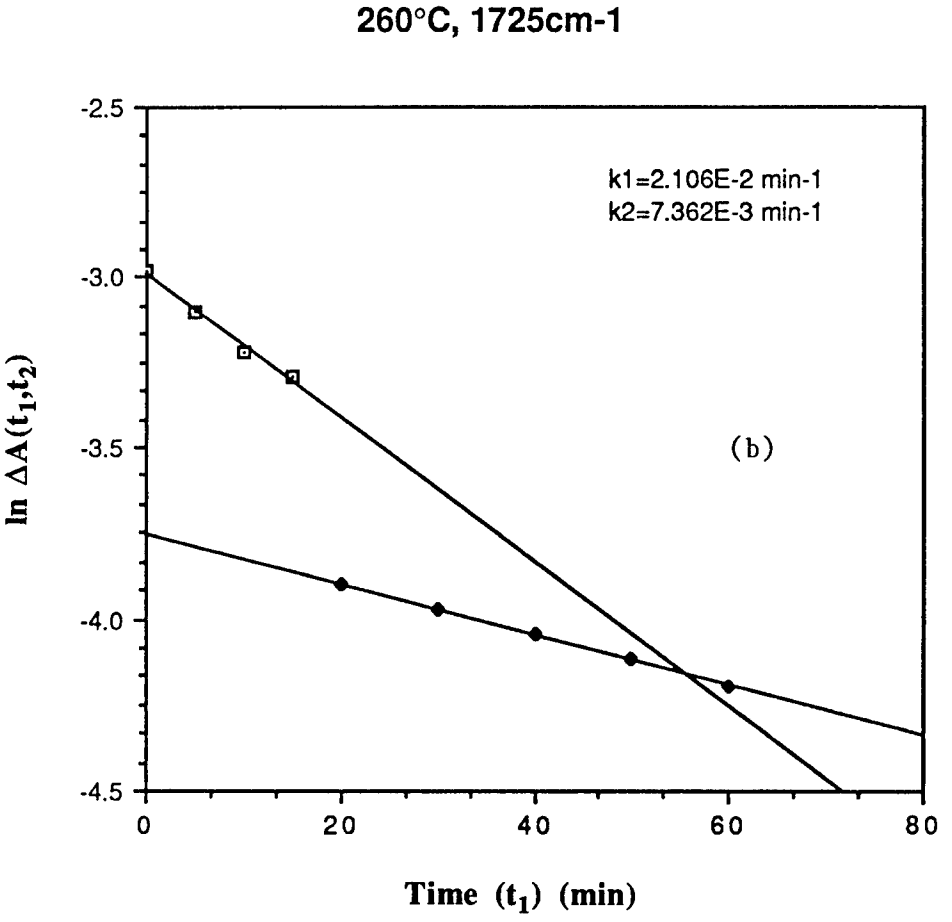


Fig.9. (continued)

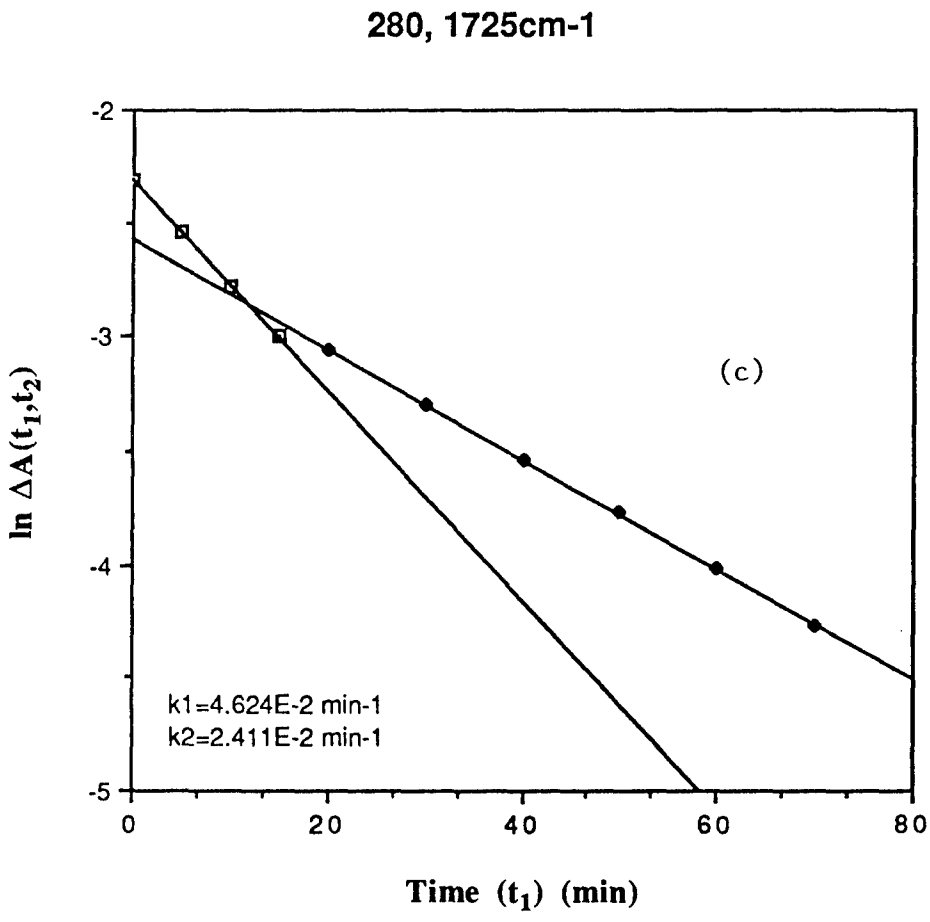


Fig.9. (continued)

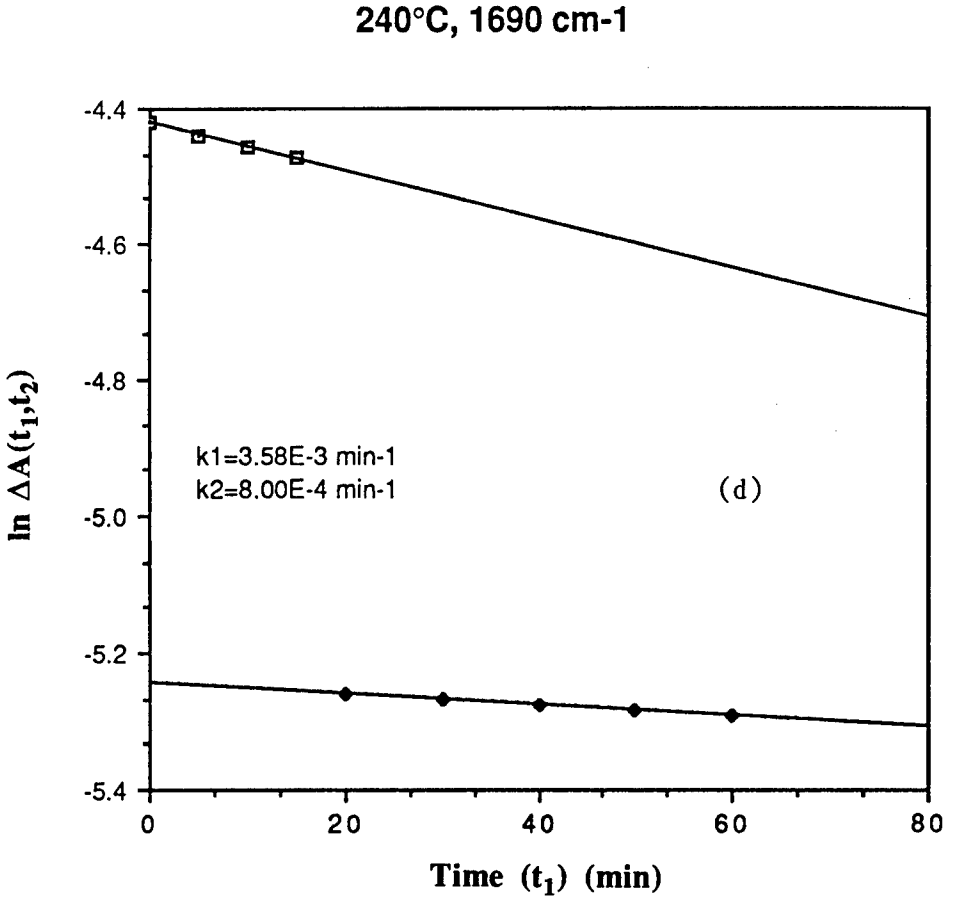


Fig.9. (continued)

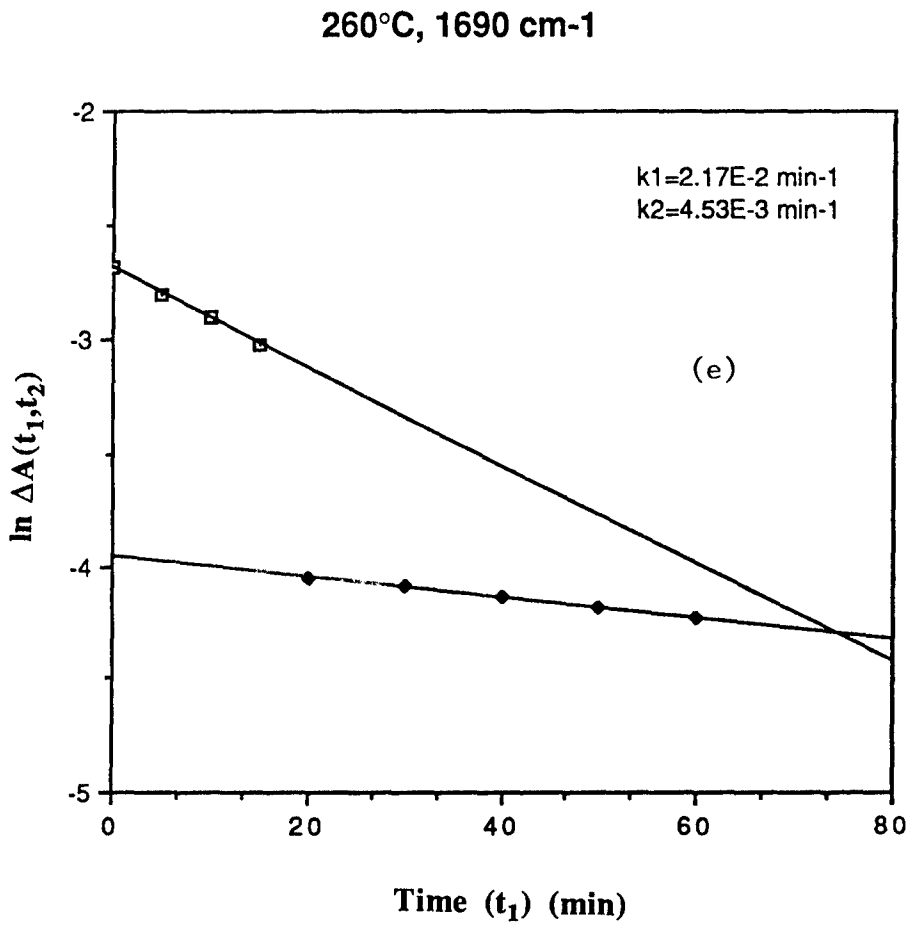


Fig.9. (continued)

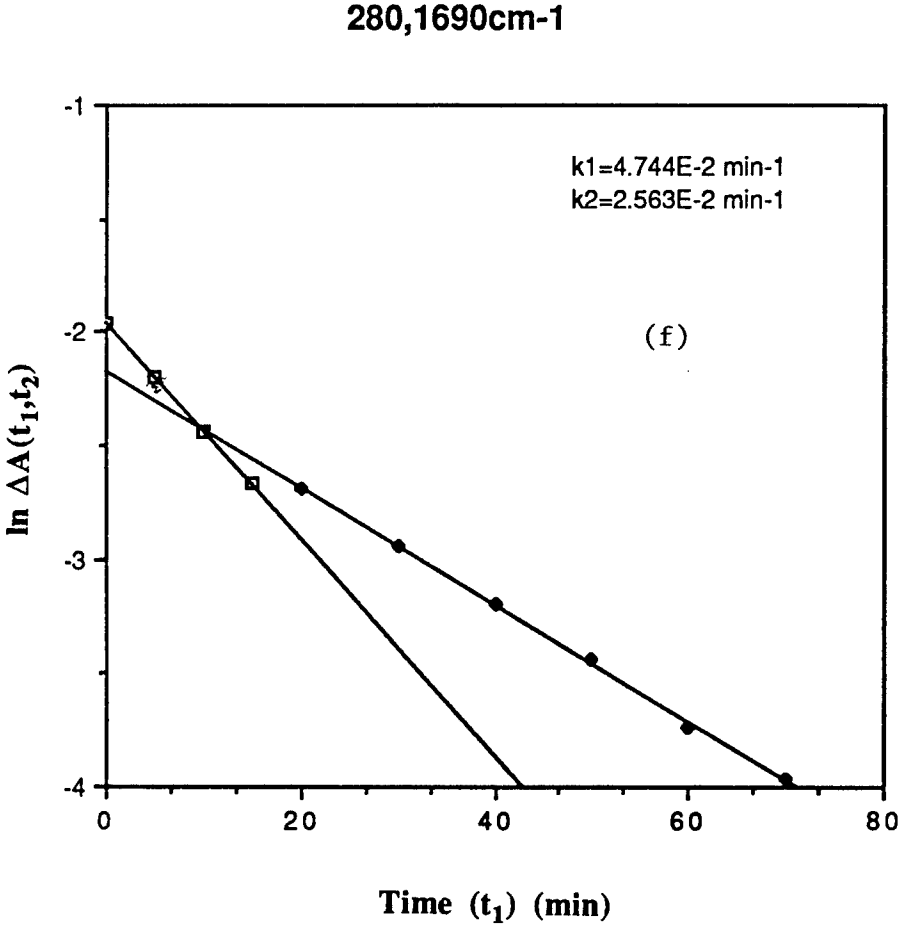


Fig.9. (continued)

Table 4. The kinetic parameters of imidization from ΔA data

(a) at 1725 cm^{-1}

k_1 (min^{-1})			k_2 (min^{-1})		
280°C	260°C	240°C	280°C	260°C	240°C
4.624E-2	2.106E-2	5.34E-3	2.411E-2	7.362E-3	9.50E-4
K_0 = 5.75 E10, E_1 = 31 Kcal/mole			K_0 = 3.19 E16, E_2 = 46Kcal/mole		

(b) at 1690 cm^{-1}

k_1 (min^{-1})			k_2 (min^{-1})		
280°C	260°C	240°C	280°C	260°C	240°C
4.744E-2	2.17E-2	3.58E-3	2.563E-2	4.53E-3	8.00E-4
K_0 = 1.57 E13, E_1= 37 Kcal/mole			K_0 = 4.72 E10, E_2= 49 Kcal/mole		

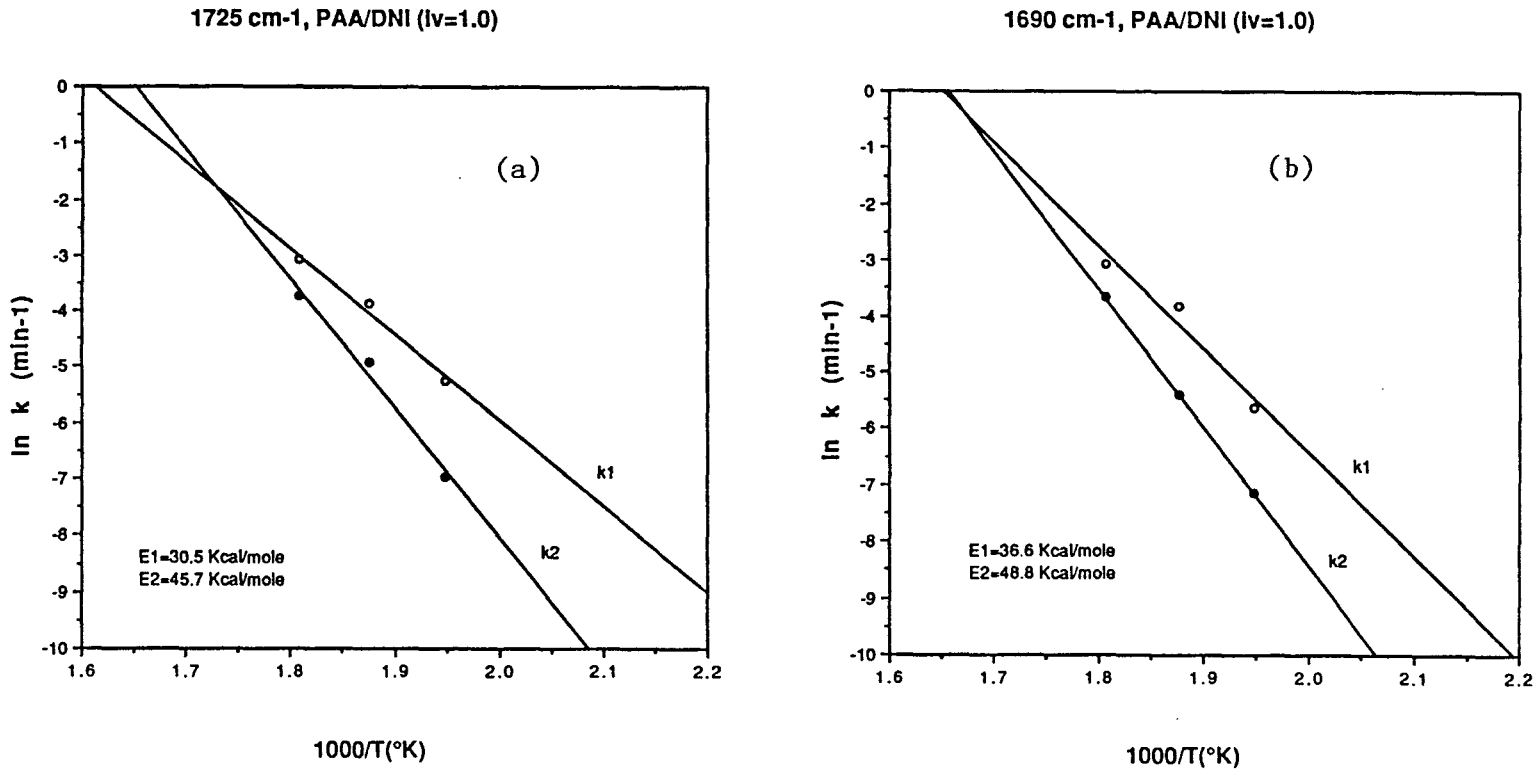


Fig.10. Arrhenius plot for imidization of PAA/DNI-3A at (a) 1725, and (b) 1690 cm^{-1}

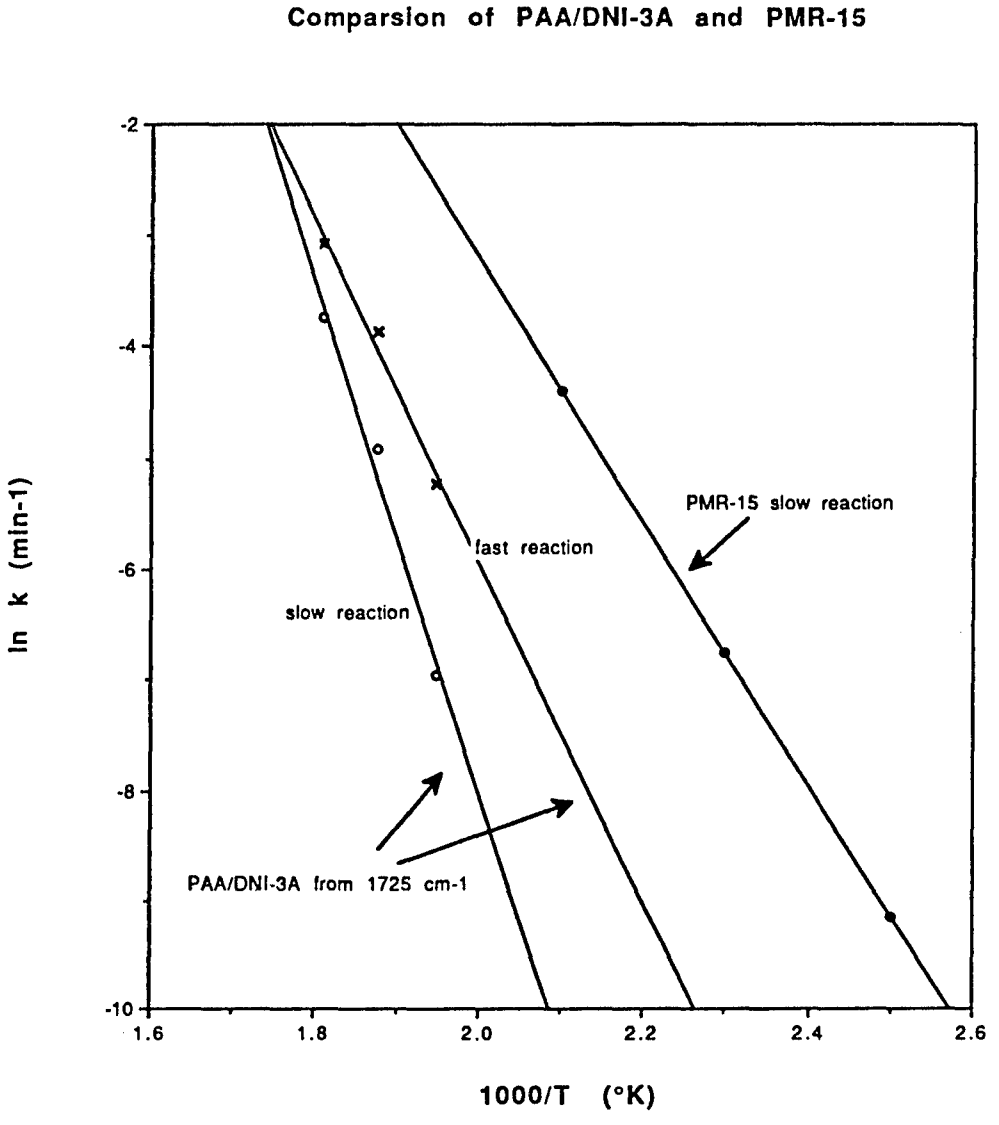


Fig.11. Comparison of Arrhenius plot for imidization of PAA/DNI-3A and PMR-15

shown in the same report, the author [15] did point out that the fast reaction constants should be one to three orders of magnitude larger than the rate constants of the slower reaction. This large difference of rate constants did not happen in the PAA/DNI-3A systems since the reaction kinetics was controlled by the system viscosity and the viscosity change during the solid state processing for PAA/DNI-3A is not very significant compared to the PMR systems. Furthermore, from Fig.11, it shows that for the PAA/DNI-3A system the k curves have steeper slopes and are located in the higher temperature range for similar k values than for the PMR systems. This means that the PAA/DNI-3A systems have much smaller processing window and also only in a shorter higher temperature range can the reaction occur in a reasonable rate.

4.6 The TICA Results and Correlation with the Two Kinetic Rates

The TICA experiments were conducted with RDS in both cure mode and isothermal scans. The results are shown in Figs.12a-12c. The cure scan illustrated that the material began to soften at about 200°C and the softening rate is very slow. At 250°C the viscosity reached the minimum and increased again due to additional reaction. The softening window was very narrow.

The isothermal scans were conducted at 280 and 240°C respectively. The moduli curves from both temperature scans showed the typical softening at the beginning, followed by the vitrification process. The FTIR kinetic results showed that there were two reaction rates associated with the ring closure reaction, a fast reaction (k_1) at the beginning followed by a slower rate (k_2). Clearly, this change in rate was related to the rheology of the material. When the material was in the softening stage, the reaction proceeded according to rate k_1. After the system vitrified, the glassy state rheology slowed down the conversion rate, and the remaining conversion proceeded according to rate k_2.

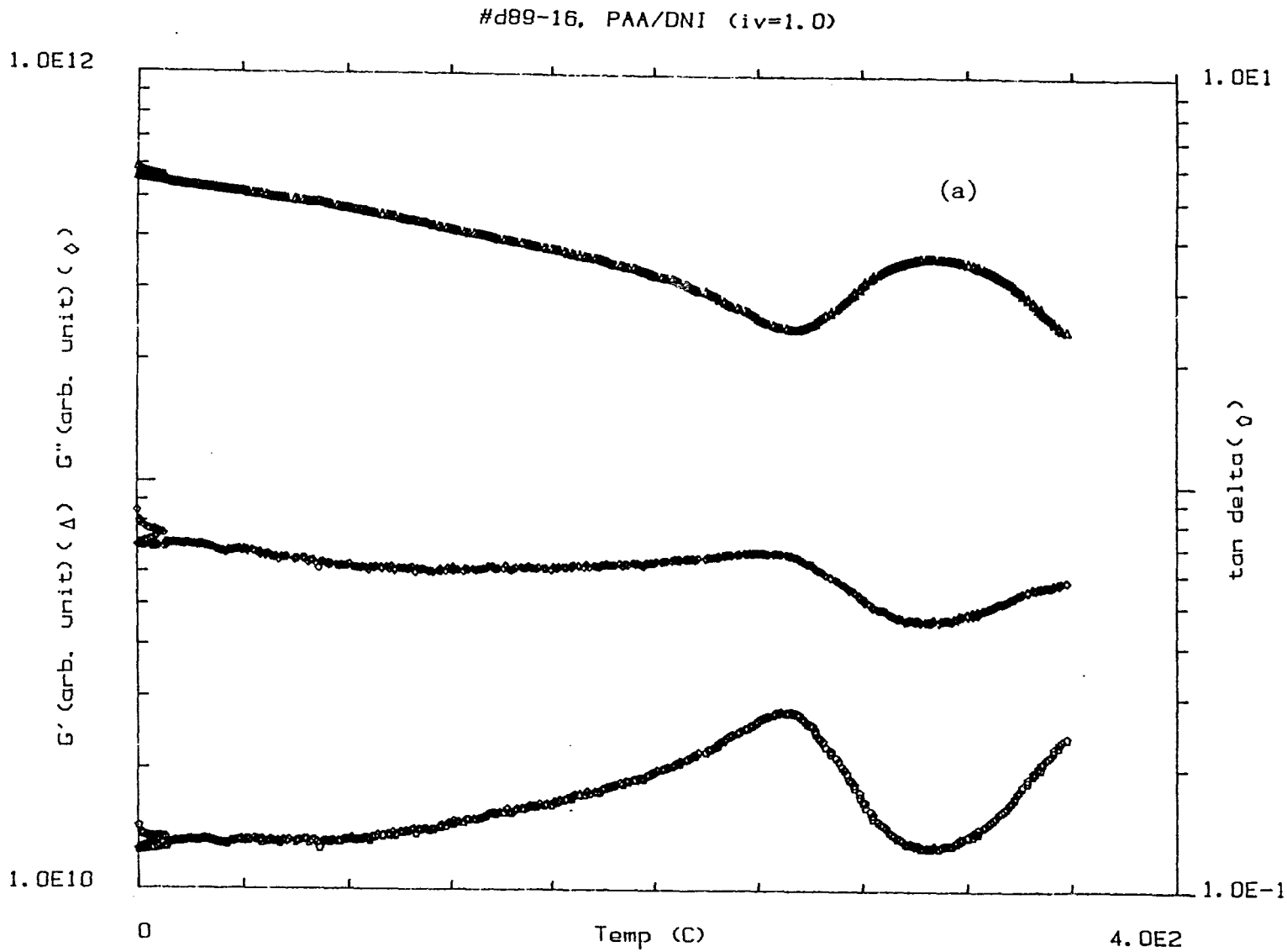


Fig.12. TICA spectra of PAA/DNI-3A for (a) temperature scan, and (b) isothermal scan at 240°C, and (c) isothermal scan at 280°C

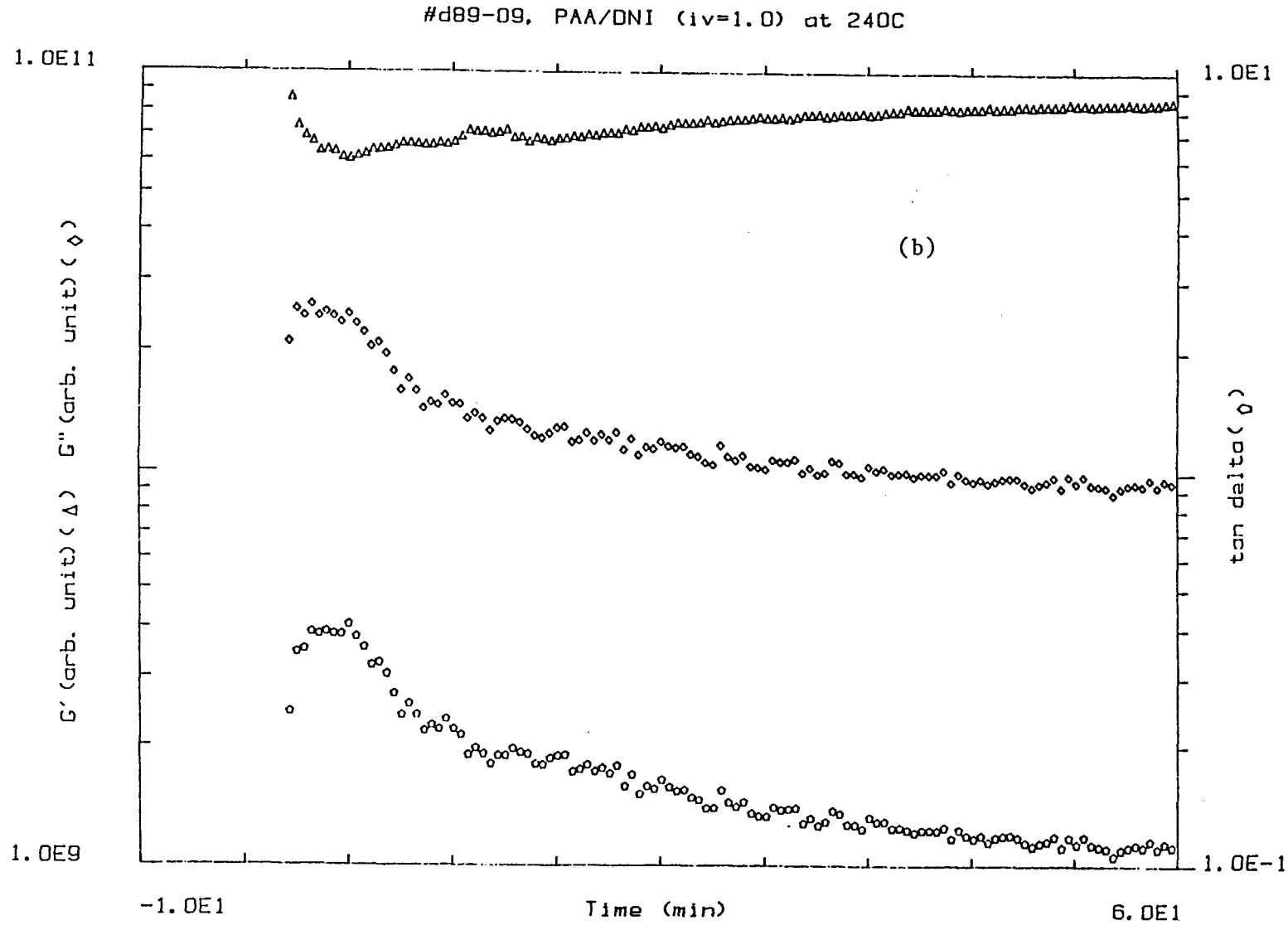


Fig.12. (continued)

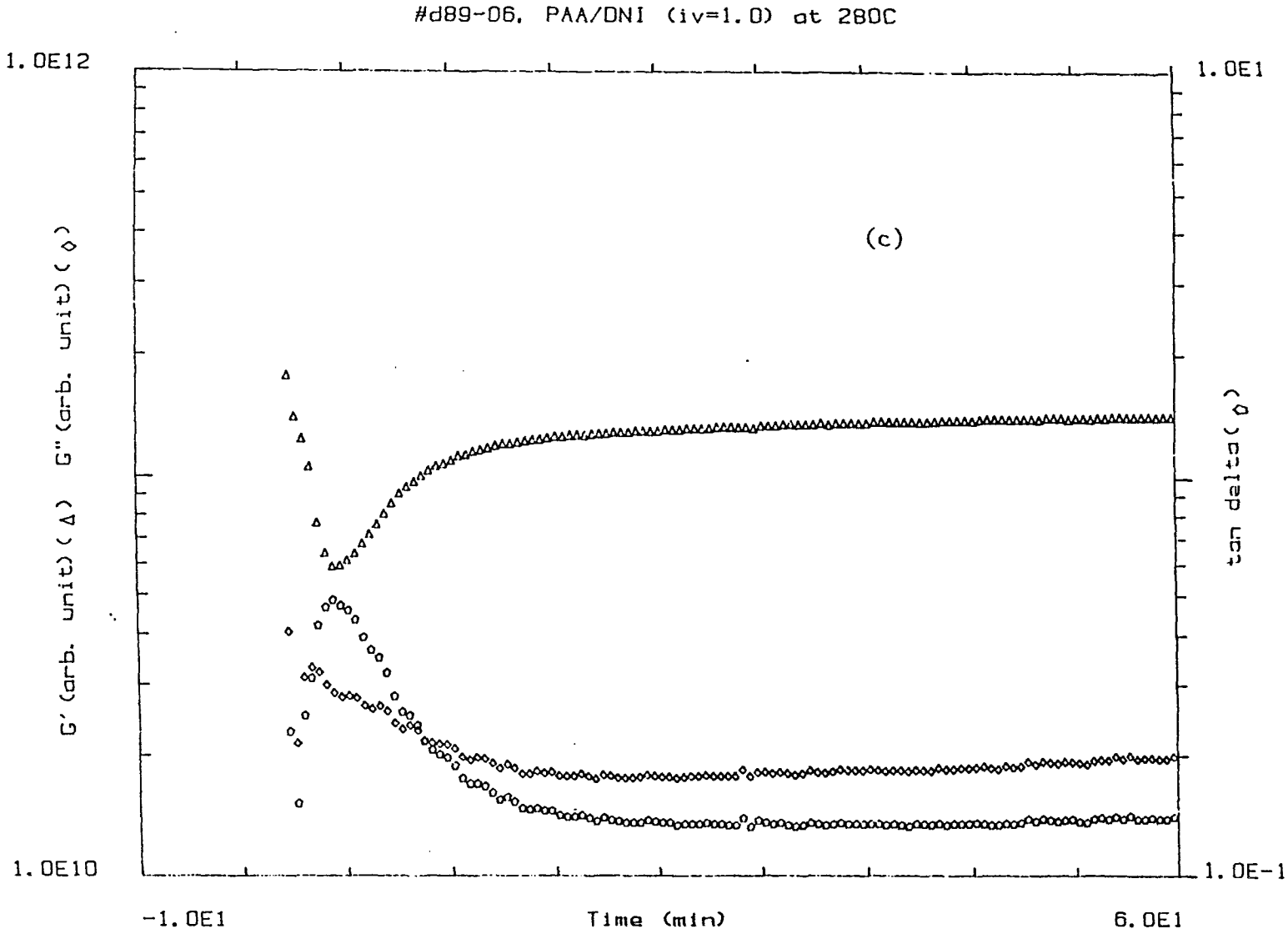


Fig.12. (continued)

To illustrate the relationship between the softening and the reaction rates, the TICA and FTIR data were replotted in Fig.13. It is very clear that the fast reaction is associated with the softening region. After the material vitrified at time t=12 minutes, the reaction rate assumed the k_2 value.

Processing Consideration of In-Situ Rod Formation

(a) TICA rheology

(b) kinetics from IR

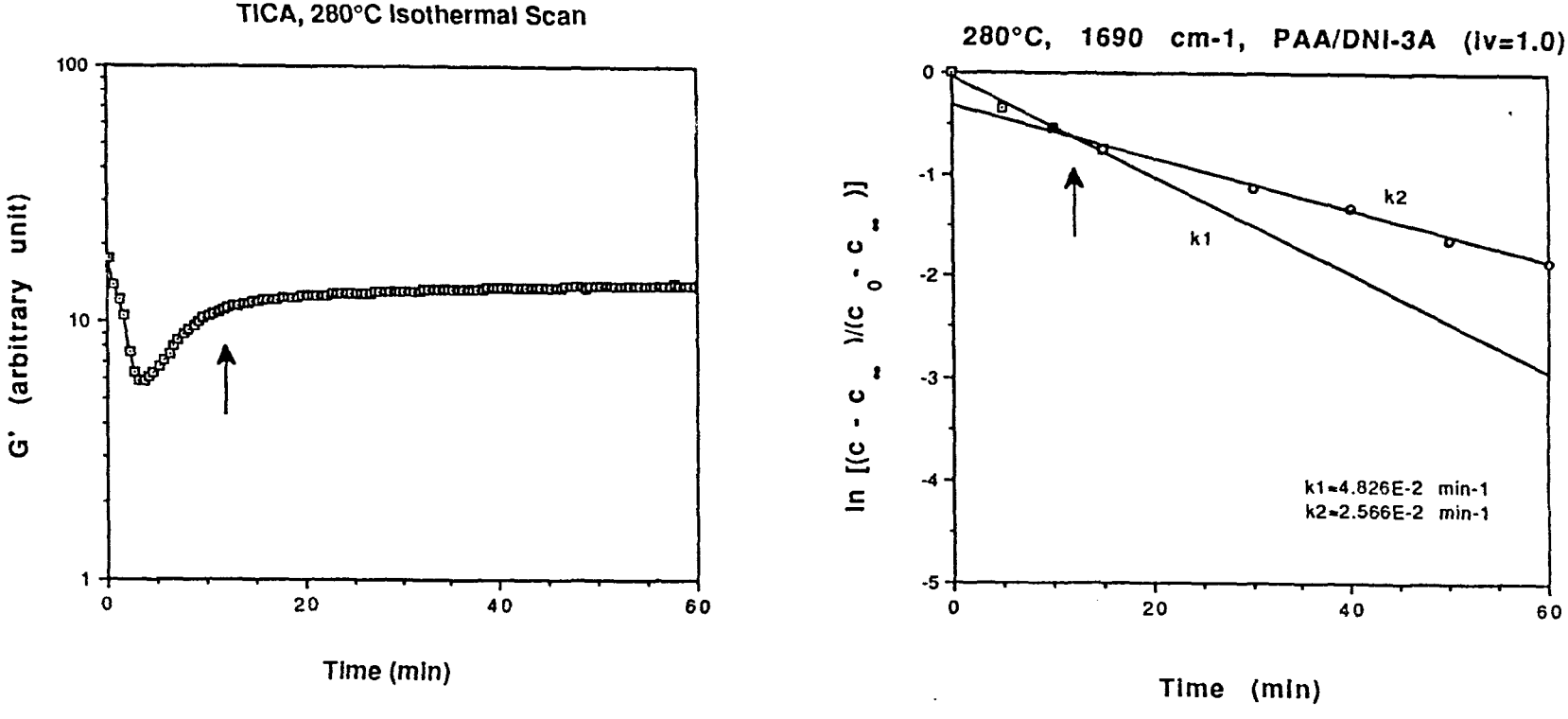


Fig.13. Relationship between softening and reaction rate for PAA/DNI-3A

SECTION 5

SUMMARY

The rod conversion kinetics of the PPA/DNI-3A system was studied using the FTIR. Analysis of the isothermal 280°C FTIR data showed a nice correlation between the disappearance of amic amide and the formation of imide, indicating a direct conversion without intermediate. The activation energy obtained for the poly(amic amide) was substantially higher than the literature value of amic esters. The isothermal results showed that the conversion proceeded initially according to a fast reaction rate k_1 and slowed to a different reaction rate k_2 later. The crossover point between k_1 and k_2 corresponds nicely with the vitrification time of the rheology measurement. This proves that the conversion rate and possibly the degree of conversion, is rheologically controlled.

This study defined the kinetic parameters of the rod conversion reaction at the beginning of the reaction. The effect of the crosslinking chemistry was not studied. The cracking of the nadic end group into cyclopentadiene presented a complication in the study of the crosslinking effect. The cyclopentadiene evolution temperature range overlapped with the rod conversion reaction range. Another crosslinking chemistry will be more suitable to study the crosslinking effect on rod conversion.

REFERENCES

1. L.S. Tan and F.E. Arnold, "In Situ Molecular Composites I: Concept and Synthesis of Dialkylamines and N-Ethyl Benzylamines Containing Ethynyl, Phenylethynyl, Nadic and Benzocyclobutenyl Groups", Polymer Preprints, 32(1), (1991).

2. L.S. Tan and F.E. Arnold, "In Situ Molecular Composites II: Synthesis and Characterization of Poly(amic Dialkylamides) Impregnated with Thermosettable Secondary Amines", Polymer Preprints, 32(1), (1991).

3. L.S. Tan and F.E. Arnold, Polymer Preprints, 28(2), p316 (1987)

4. L.S. Tan and F.E. Arnold, "A Convenient Synthesis of High Molecular Weight Poly(amic Dialkyl Amide)", Polym. Preprint, p316 (1988)

5. C.Y-C Lee and I.J. Goldfarb, "Torsion Impregnated Cloth Analysis (TICA): A Forced Torsion Technique to Study Resins Supported by Inert Substrate", Polym.Engr, & Sci., 21, p390 (1981).

6. T.T. Serafini, P.Delvigs and G.R. Lightsey, U.S. Patent 3,745,149 (1973)

7. M.J. Brekner and C. Feger, "Curing Studies of a Polyimide Precusor", J. Polym. Sci., A, 25, 2005 (1987). "Curing Studies of a Polyimide Precusor. II. Polyamic Acid", ibid, A, 25, 2479 (1987).

8. C. Feger, "Curing of Polyimides", Polym. Eng. Sci., 29 (5), p347 (1989)1b. T.L. St. Clair, M.K. Gerber and C.R. Gautreaux, "A comparion of the Polyimide isomers PMDA/ODA and ODPA/p-PDA", ACS (PMSE), Spring, 1989, p.183.

9. P.D. Frayer,"The Interplay Between Solvent Loss and Thermal Cyclization in LARC-TPI", in "Polyimides -I" edited by K.L. Mittal, Plenum Press (1984)

10. E.L. Johnson, "The Effects of Reaction Temperature and Hydrolysis on Polyamic Acids and Polyimides", J. Appl. Polym. Sci., 15, p.2825 (1971)

11. C-P Yang and S-S Wang, "Studies on the Imidization of N-Substituted Polymleamis Acids", J. Polym Sci." A27, p15 (1989)

12. J.A. Kreuz, A.L. Endrey, F.P. Gay, and C.E. Sroog, "Studies of Thermal Cyclizations of Polyamic Acids and Tertiary Amine Salts", J. Polym Sci., A-1(4), p2607 (1966)

13. L.A. Laius, M.I. Bessonov, Ye. V. Kallistova, N.A. Adrova, and F.s. Florinskii, "Infrared Spectral Absorption Study of the Formation Kinetics of Polypyromellitimide (PPMI), Vysokomol. soyed. A9(10), p2185 (1967)

14. L.A. Lauis and M.I. Tsapovetsky, "Kinetics and Mechanism of Thermal Cyclization of Polyamic Acids", Polymide I,edited by K.L.Mittal, Plenum Press, NY, 1984

15. R.W. Lauver, "Kinetics of Imidization and Crosslinking in PMR Polyimide Resin", J. Polym. Sci., Poly. Chem. edition, 17, p2529 (1979).

16. F.A. Myers, "Cure Theology of PMR-15 Prepreg", Second International Technical Conference on Polyimides (1985)

17. R.W. Snyder and P.C. Painter, "Dynamic FT-IR Analysis of Cure Reactions and Kinetics of Polyimides", PMSE Proc. (Amer. Chem. Soc.), p57, 1988

18. J.D. Summers and J.E. McGrath, "Kinetic Studies of Homo- and Copolymer Solution Imidization", Polym. Preprints, 28(2), p230 (1987)

19. E.D. Wachsman and C.W. Frank, "Effect of Cure History on the Morphology of Polyimide: Flurescence Spectroscopy as a Method for Determining the Degree of Cure", Polym. Matl. Sci. Eng. Proceeding (Amer. Chem. Soc.), p46, 1988

20. N.G. Gaylord and M. Martan, "Homopolymerization of Isomeric n-Phenyl-5-Norbornene-2,3-Dicarboximides, Model Compounds for Norbornene End-Capped Addition-Curing Polyimides", Polym. Preprint, 22, p11 (1981)

21. D.A Scola, in Processding of Second International Polyimide Conference, Society of Plastic Engineers, 1985, p247-252.

22. M.Navarre,"polyimide Thermal Analysis", in "Polyimides I" edited by K.L. Mittal, Plenum Press, 1984

23. E. Sacher, "A Reexamination of Polyimide Formation", J. Macromol. Sci.-Phys., B25(4), p405 (1986)

24. M.M. Koton et al, "Investigation of the Kinetics of Chemical Imidization", Polym. Sci. (USSR), 24, p791 (1982).

25. D.Garcia and T.T.Serafini, "FTIR Studies of PMR-15 Polyimides", J.Polym.Sci., B25, p2275 (1987).

26. P.R.Young and A.C. Chang, "FTIR Characterization of Thermally Cycled PMR-15 Composites", 33rd International SAMPE Symposium (1988).

27. C.A. Pryde, J Polym.Sci., "IR Studies of Polyimides. I. Effects of Chemical And Physical Changes During Cure", A(27), p711 (1989)

28. J.D. Summer et al., "Synthesis and Characteristics of Novel Poly(imide Siloxane) Segmented Copolymers, Polymer Preprints, 27, (1986)

29. J.D. Summers, Et al.," Synthesis and solution Imidization Studies of Soluble Poly(imide siloxane) Segmented Copolymers", 32nd Intern. SAMPE Symp. (1987)

30. G.Socrates, "Infrared Characteristic Group Frequencies", Chap. 10, John-Wiley & Sons, NY 1980.

APPENDIX A

Illustrated examples for kinetic data calulation from Sections 3(c) and 3(d)

Example 1 For a fisrt order reaction, $[c]_t = [c]_0 \exp(-t/100)$ then k=0.01, the [c] values at different time t are listed in the following table.

time (min)	$[c]_t/[c]_0$
0	1.00
5	0.95123
10	0.90484
15	0.86071
...	
120	0.30119
180	0.16530

If the data were analyzed by assuming $[c]_t$ at t=120 min to be zero ($[c]_{120}$ =0) and apply equation (10) to get the k value the error is about 70% (k=0.017), if $[c]_{180}$ is assumed to be zero the error is reduced to 50% (k=0.015). Because of other complication in solid state reaction like diffusion controlled quenching of the reaction, it is difficult to determine if $[c]_t$ is indeed zero. That is the motive to develop the approach for evaulating the k values, in which whether t is equal to infinity or not is not involved at all.

The same example is used to demonstrate the application of this approach as follows.

Example 2.

For the same first order reaction $[c]_t = [c]_0 \exp(-t/100)$, assume $a_C\ b = 1$. Then

$$A_C(t) = a_C\ b\ [c]_t = [c]_t$$

and

$$\Delta A(t_1, t_2) = \Delta A_c(t_1, t_2) = [c]_{t_1} - [c]_{t_2} = \Delta[c]$$

The concentration, concentration difference and its logarithm values are listed in the following table.

time (min)	$[c]_t/[c]_0$	$\Delta[c]_t/[c]_0$	ln $\Delta[c]_t/[c]_0$
0	1.00	0.049	-3.021
5	0.95123	0.046	-3.071
10	0.90484	0.044	-3.121
15	0.86071		
...			
120	0.30119		
180	0.16530		

After plotting (ln $\Delta[c]_t/[c]_0$) or (ln $\Delta A(t_1,t_2)$) verse time t_1, the slope was found to be exactly equal to the true k value, 0.01.

Two things have to be emphasize. Firstly, it is ploted of (ln $\Delta[c]_t/[c]_0$) or (ln $\Delta A(t_1,t_2)$) verse t_1, not verse other t. Secondly, it has to be equally spaced data used. Non equally spaced data do not fit equation (12). This technique is very useful for analyzing FTIR spectra. No infrared absorbance due to the unidentified background or the initial product is involved here. With the data treatment shown in this approach the correct kinetic data k can then be obtained.

APPENDIX B

The Report of TGA/MS Results of PAA/DNI-3A and DNI-3A Systems from SRL

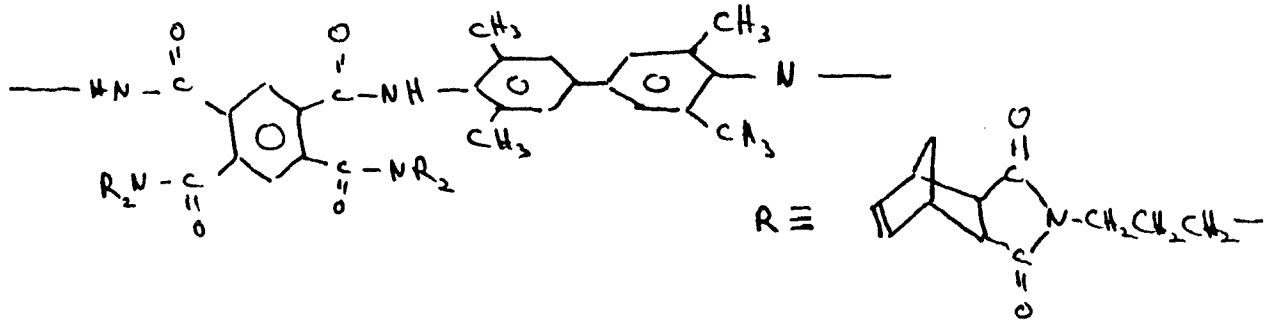
SYSTEMS RESEARCH LABORATORIES
2800 INDIAN RIPPLE RD., DAYTON, OH 45440-3696 • (513) 426-6000
A DIVISION OF ARVIN/CALSPAN

8 August 1989

In Reply Reference: 5556

Wright Research and Development Center
Materials Laboratory
WRDC/MLBP (Attn: Lisa R. Denny)
Wright-Patterson Air Force Base, OH 45433-6533

SUBJECT: Analysis of Sample LST-70359-44A



1. Initial Weight 4.3 mg
   Weight Loss (950°C) 2.8 mg (65%)

2. The temperature dependence of the total-ionization current is shown in Fig. 93. The behavior of dW/dT provides no information due to noise in the data. This is the fifth sample in this series where dW/dT data are poor (c.f., LST-70357-19A, LST-70359-5A, -13A, -13B). One possible explanation is swinging of the sample which is induced by the rapid loss of C_5H_6. The overall weight loss in this sample falls in the range (51 - 68%) established from the previous three samples.

   Two major maxima in the total-ionization profile occur at 230 and 370 °C; these are essentially as observed for Sample LST-70357-19A.

3. At temperatures below 230°C, only traces of products are observed. Three profiles can be discerned; however, the low abundance of these products precludes assignment. The peak in the total-ionization current at 230°C arises from the release of C_5H_6 as the product of the retro-Diels Alder reaction. No other products are released in this temperature region.

4. The next volatile product arises from the imidization process. The rate of its production maximizes at 370°C and accounts for the second peak in the total-ionization spectrum. Although it is not possible to make positive identification of the structure, it can be said that it is a complex secondary amine. The highest mass ion observed is at m/e 189; the largest major ion is at m/e 138 and is tentatively assigned as

   $$C_3H_6NC_3H_5N{=}C{=}O$$

   Since no other volatiles of any magnitude are seen following the retro-Diels Alder reaction prior to the imidization, it is possible that the amine cyclizes prior to undergoing the imidization. No molecular ion is observed corresponding to the nominal mass of the diamine expected from the retro-Diels Alder reaction. Since all ions in this region have the same temperature dependence, it is concluded that a single secondary amine is being observed which is not degraded thermally but by electron impact during detection.

5. Other identified products (thermal degradation) include CO, CH_4, H_2, HCN, and tetramethyl-substituted biphenyl.

6. The temperature dependence of the identified products is shown in Figs. 94 and 95.

Very truly yours,

SYSTEMS RESEARCH LABORATORIES, INC.
A Division of Arvin/Calspan

E. Grant Jones, Ph.D.
Senior Chemist
Research Applications Division

EGJ:mw

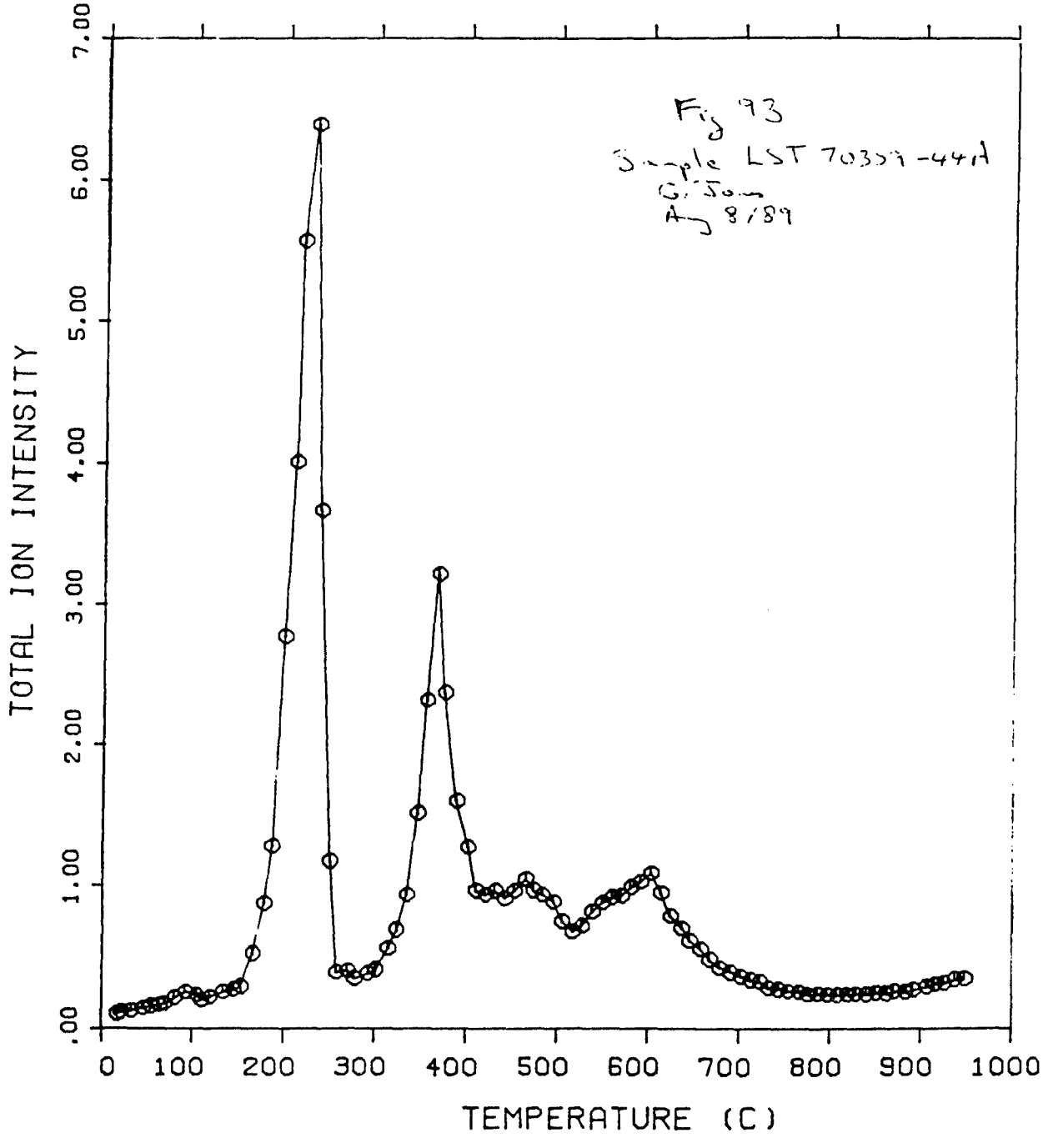
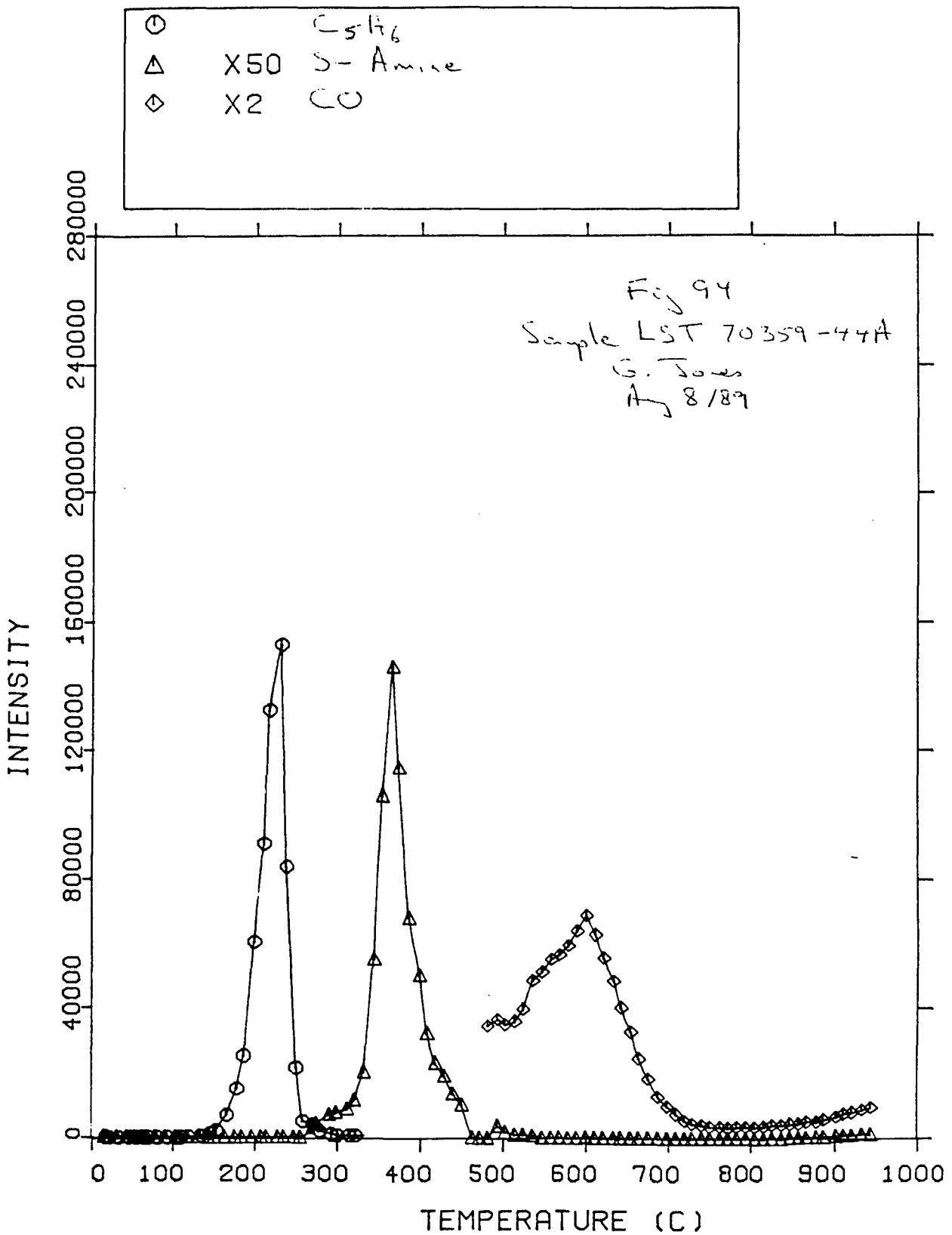
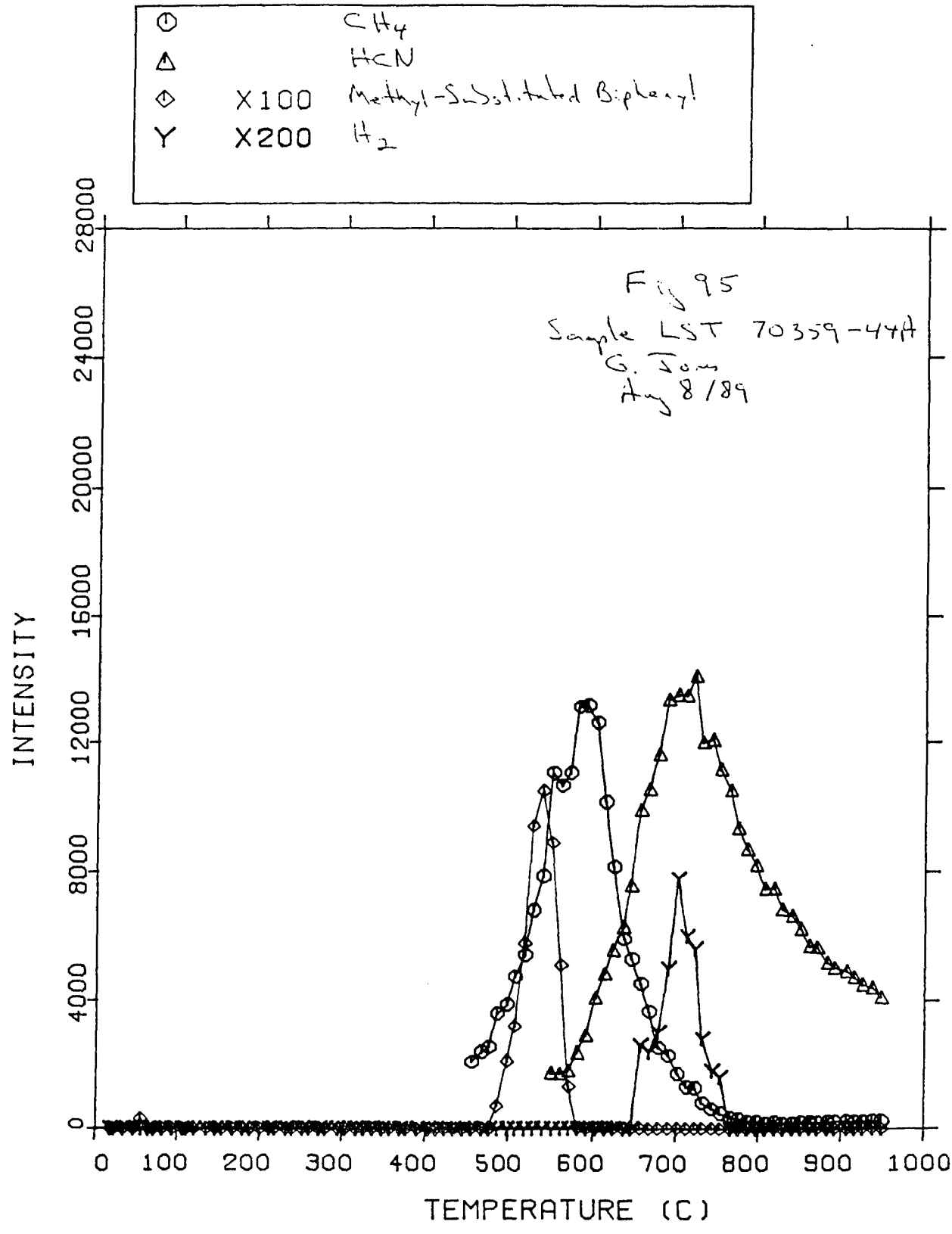


Fig 93
Sample LST 70359-44A
G. Sam
A 8/89
TOTAL ION INTENSITY
.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
0
100
200
300
400
500
600
700
800
900
1000
TEMPERATURE (C)


C5H6
X50 S- Amine
X2 CO
Fig 94
Sample LST 70359-44A
G. Jones
8/89
INTENSITY
0
40000
80000
120000
160000
200000
240000
280000
0
100
200
300
400
500
600
700
800
900
1000
TEMPERATURE (C)


CH4
HCN
X100 Methyl-Substituted Biphenyl
X200 H2
Fig 95
Sample LST 70359-44A
G. Tom
Aug 8/89
INTENSITY
0
4000
8000
12000
16000
20000
24000
28000
0 100 200 300 400 500 600 700 800 900 1000
TEMPERATURE (C)

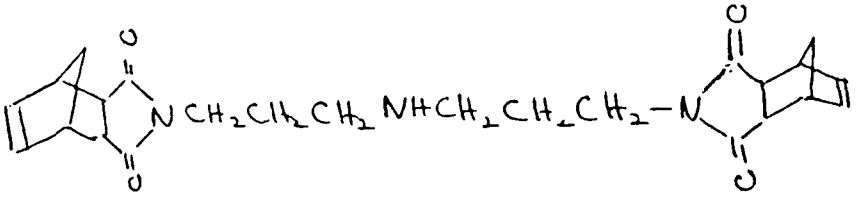
SYSTEMS RESEARCH LABORATORIES
2800 INDIAN RIPPLE RD., DAYTON, OH 45440-3696 • (513) 426-6000
A DIVISION OF ARVIN/CALSPAN

15 August 1989

In Reply Reference: 5556

Wright Research and Development Center
Materials Laboratory
WRDC/MLBP (Attn: Lisa R. Denny)
Wright-Patterson Air Force Base, OH 45433-6533

SUBJECT: Analysis of Sample LST-70357-14A



1. Initial Weight 5.8 mg
   Weight Loss 5.7 mg (98%)

2. The temperature dependence of dW/dT and total-ionization current is shown in Fig. 101. The extent of weight loss and the profiles in Fig. 101 indicate that the entire sample is consumed either by degrading to produce volatiles or by sub limation of the original sample prior to thermal degradation.

3. The expected major low-temperature product, C_5H_6 from the retro-Diels Alder reaction, is several times smaller than was observed in Sample LST-70359-44A. When it is realized that the current sample has the potential to release much more C_5H_6, it becomes apparent that sublimation of the original sample is competing with C_5H_6 production and, in fact, dominates. The temperature dependence of C_5H_6, shown in Fig. 102, displays a maximum at 220°C which is about 10 deg. below the corresponding maximum from Sample LST-70359-44A. This illustrates the truncation of the retro-Diels Alder reaction due to sample loss. This process appears as a high-temperature satellite maximum in the total-ionization profile (c.f., Fig. 101).

4. The major volatile products observed from this sample are unrelated to the sample per se. The largest product is unreacted reagent $C_9H_8O_3$, accounting for the large peak in the total-ionization profile. The low-temperature region around 90 and 140°C is dominated by the solvent chloroform $CHCl_3$. This observation is surprising since the solvent reported for the original preparation was CH_3Cl.

5. At 230°C approximately 90% of the original sample weight has been lost. Analysis of volatiles at higher temperature is questionable. The profile of m/e 138 is shown in Fig. 103; this was previously ascribed (Sample No. LST-70359-44A) to the s-amine released during cyclization.

6. Over the same temperature region, a broad release occurs, accounting for the maximum in the total-ionization and dW/dT temperature profiles around 420°C. Possibly significant is the fact that this unidentified product was also observed in the companion sample (unidentified) over a narrower range.

7. It should be pointed out that for small non-polymeric systems where sublimation commonly occurs, it is important that reagents and other contaminants be removed because of their increased significance compared to the products released in reduced abundance due to competition with sublimation, i.e., a cleaner sample may improve the chances of identifying the cured products.

Very truly yours,

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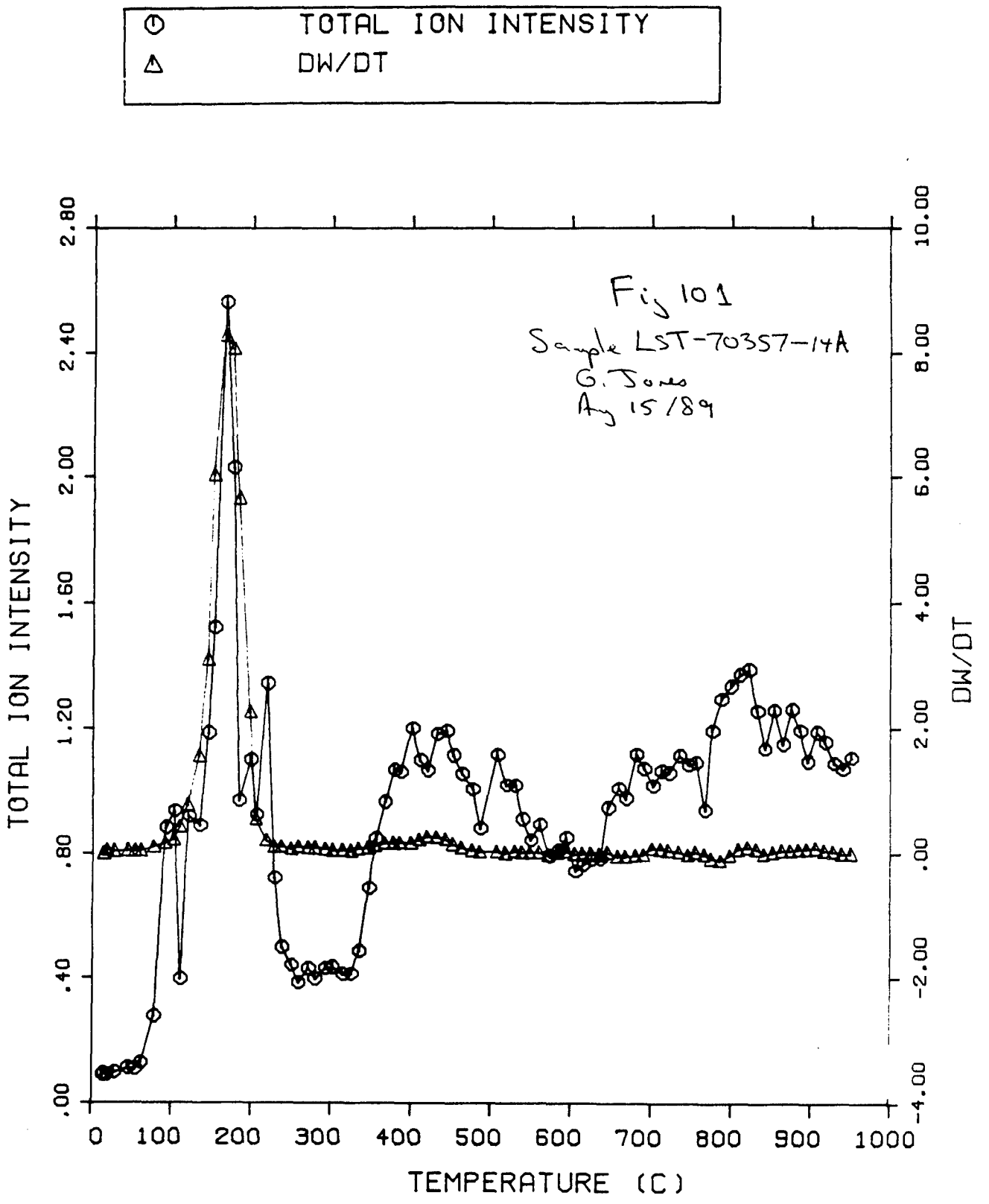
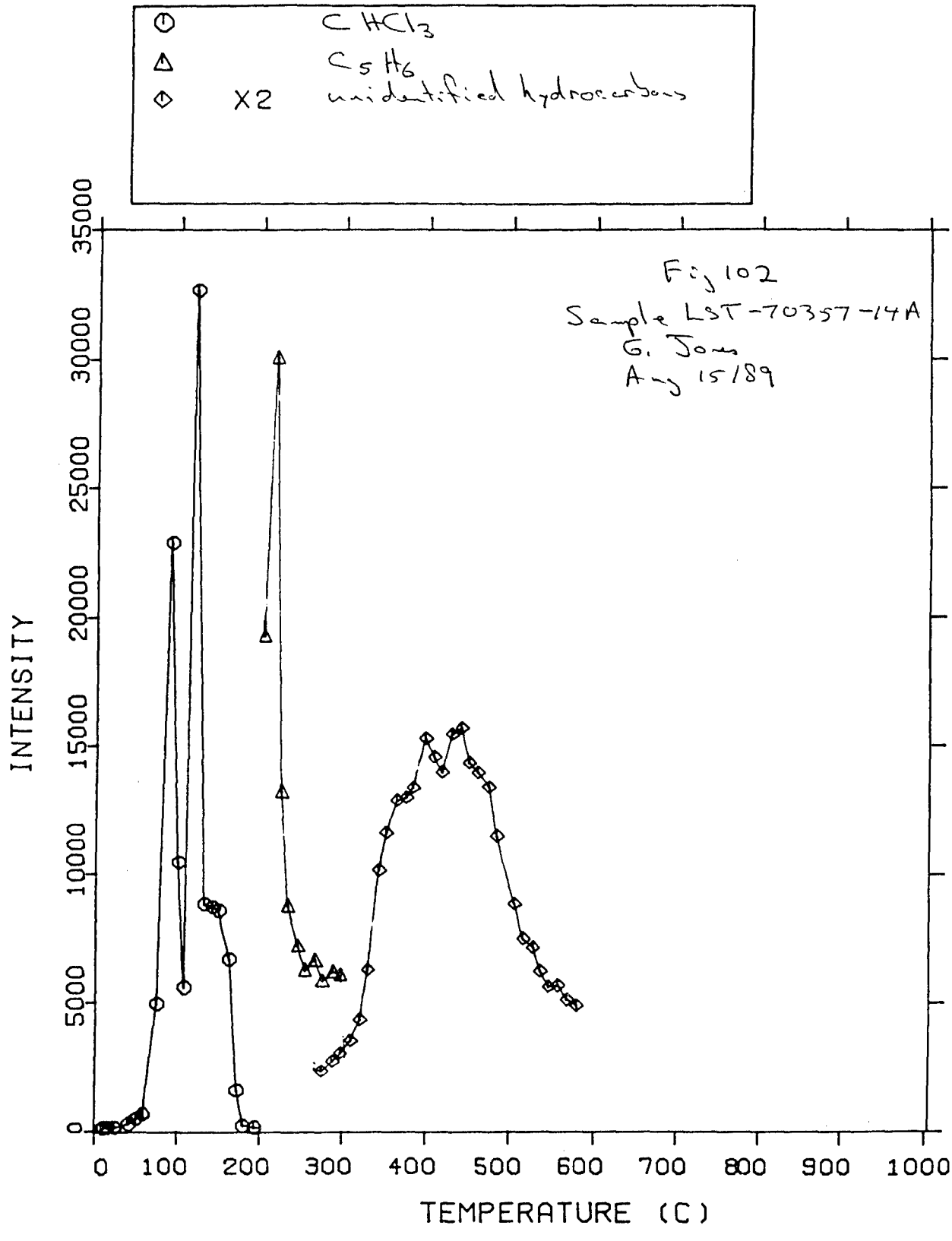
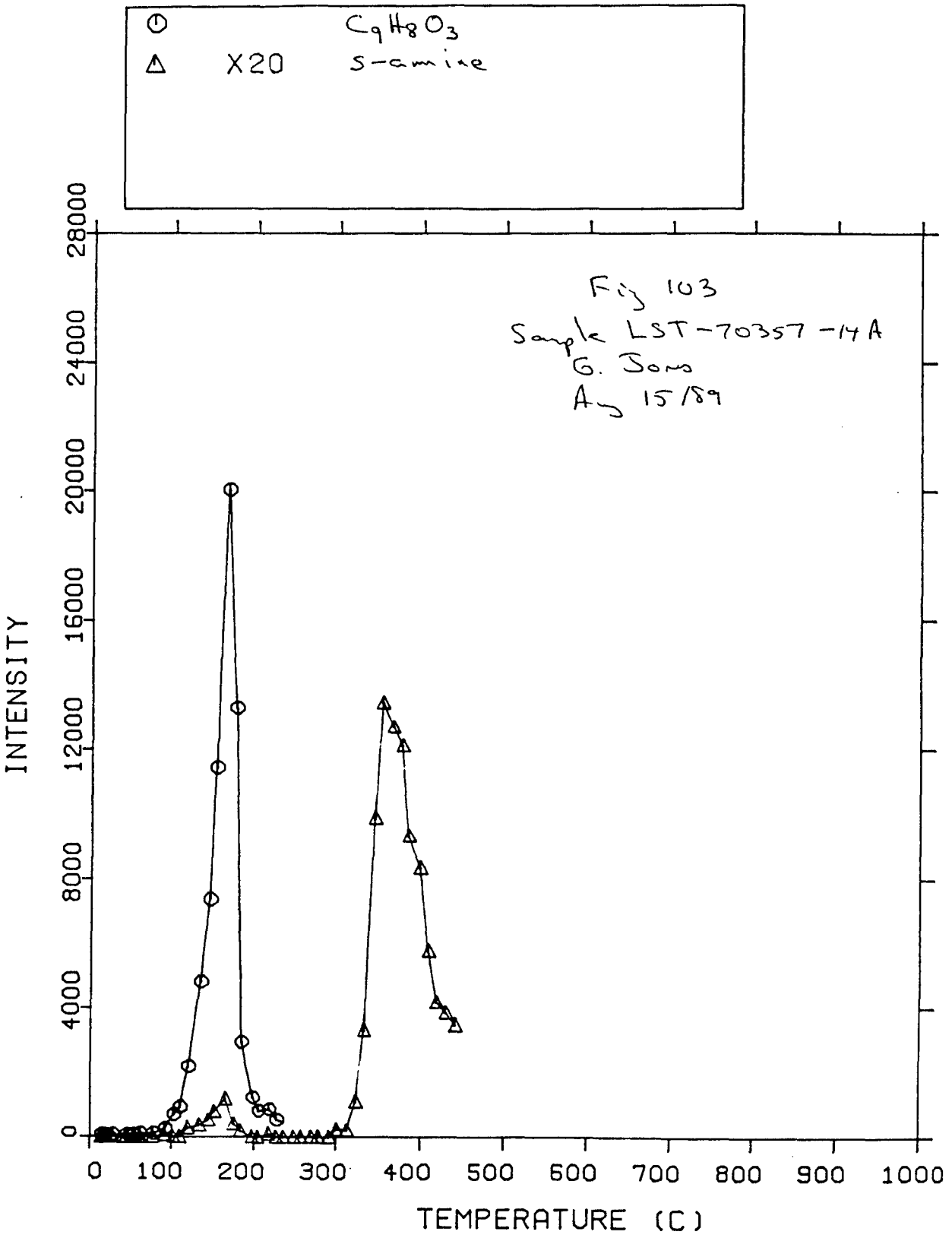
Senior Chemist
Research Applications Division

EGJ:mw


TOTAL ION INTENSITY
DW/DT
Fig 101
Sample LST-70357-14A
G. Jones
Aug 15/89
TOTAL ION INTENSITY
DW/DT
TEMPERATURE (C)
.00
.40
.80
1.20
1.60
2.00
2.40
2.80
-4.00
-2.00
.00
2.00
4.00
6.00
8.00
10.00
0
100
200
300
400
500
600
700
800
900
1000

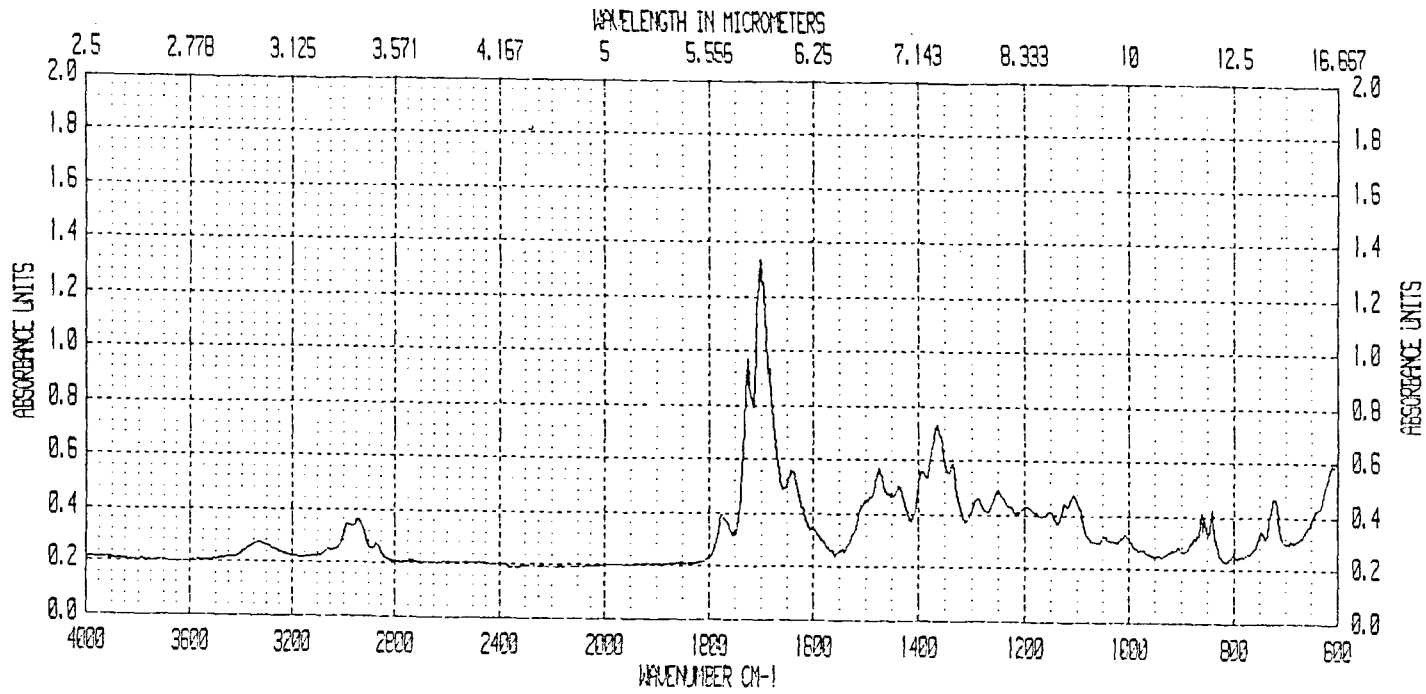

CHCl3
C5H6
X2
unidentified hydrocarbons
Fig 102
Sample LST-70357-14A
G. Jones
Aug 15/89
INTENSITY
0
5000
10000
15000
20000
25000
30000
35000
0
100
200
300
400
500
600
700
800
900
1000
TEMPERATURE (C)


C9H8O3
X20
5-amine
Fig 103
Sample LST-70357-14A
G. Soms
Aug 15/89
INTENSITY
0
4000
8000
12000
16000
20000
24000
28000
0
100
200
300
400
500
600
700
800
900
1000
TEMPERATURE (C)

APPENDIX C

Absorption Spectra from FTIR for PAA/DNI-3A

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
240/0	4 AT 240 TIME 0	no	4000.93	401.12	30 scans	0.2135

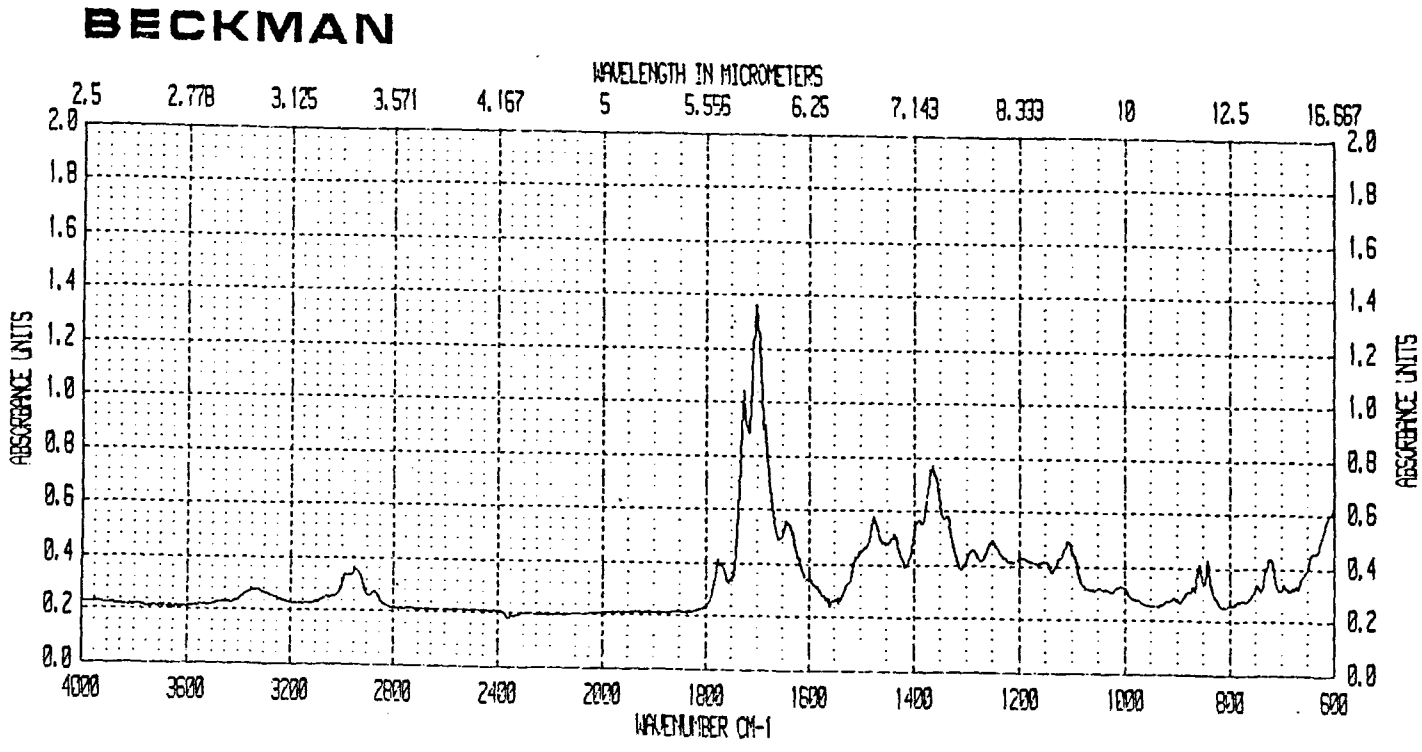


t=0 min. @240°C

BECKMAN
ABSORBANCE UNITS
WAVELENGTH IN MICROMETERS
WAVENUMBER CM-1
ABSORBANCE UNITS
2.5
2.778
3.125
3.571
4.167
5
5.556
6.25
7.143
8.333
10
12.5
16.667
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Scan Name 240/1.0
Resolu 4
Apodized no
AT 240 FOR 10 MIN
Start 4000.33
End 401.12
Scan Time 30 scans
First y 0.2145

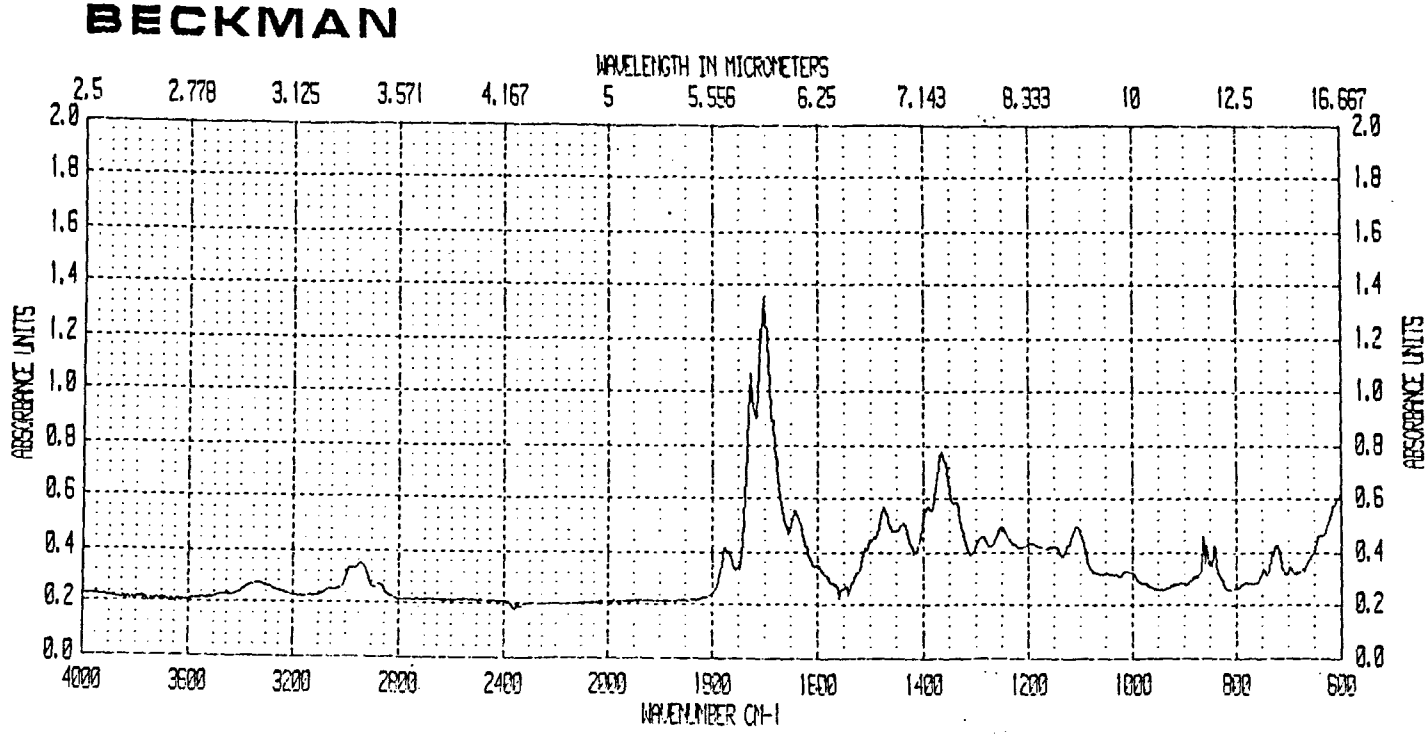
t=10 min. @240°C

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
240/20	4	no	4000.93	401.12	30 scans	0.2281
	AT 240C FOR 20 MIN					



t=20 min. @240°C

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
240/40	4	no	4000.93	401.12	30 scans	0.2277

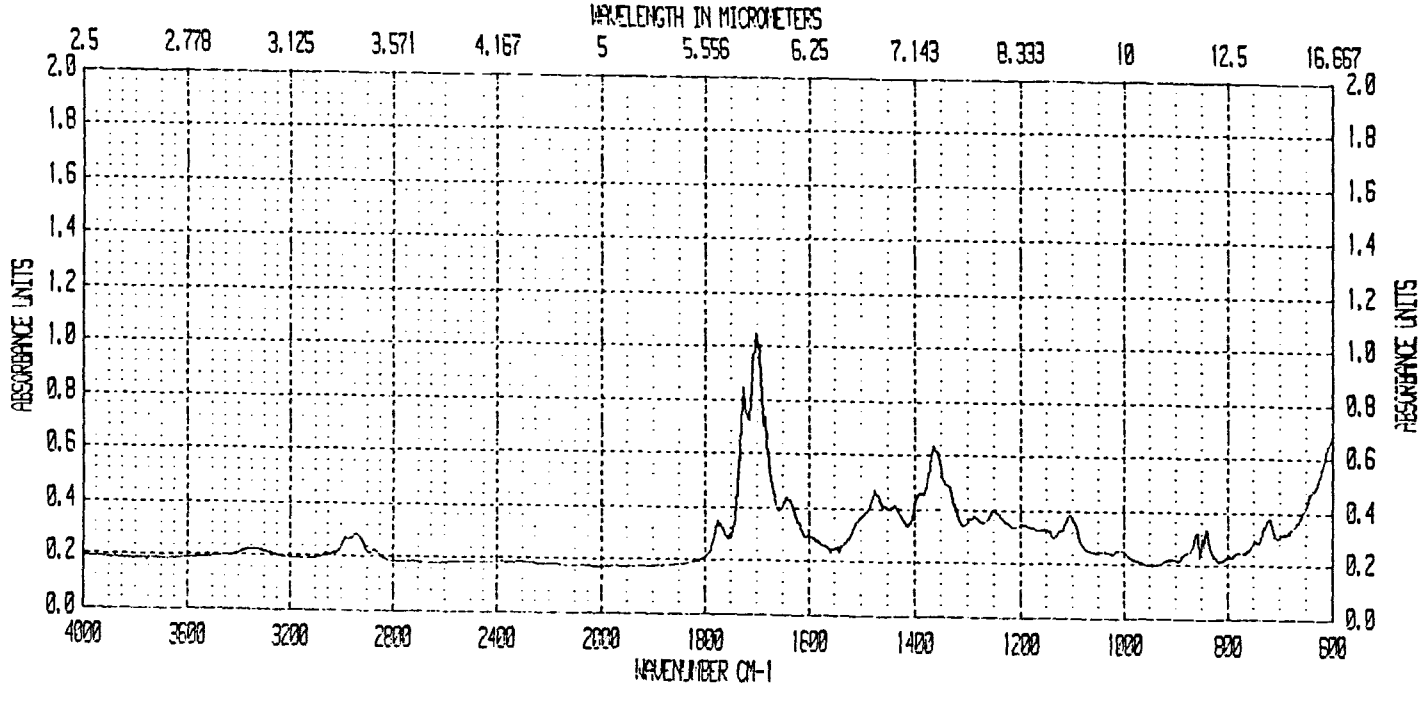


t=40 min. @240°C

BECKMAN
ABSORBANCE UNITS
WAVELENGTH IN MICROMETERS
WAVENUMBER CM-1
2.5
2.778
3.125
3.571
4.167
5
5.556
6.25
7.143
8.333
10
12.5
16.667
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
t=60 min. @240°C
Scan Name 240/60
Resolu 4
Apodized no
AT 240C FOR 60 MIN
Start 4000.93
End 401.12
Scan Time 30 scans
First Y 0.2322

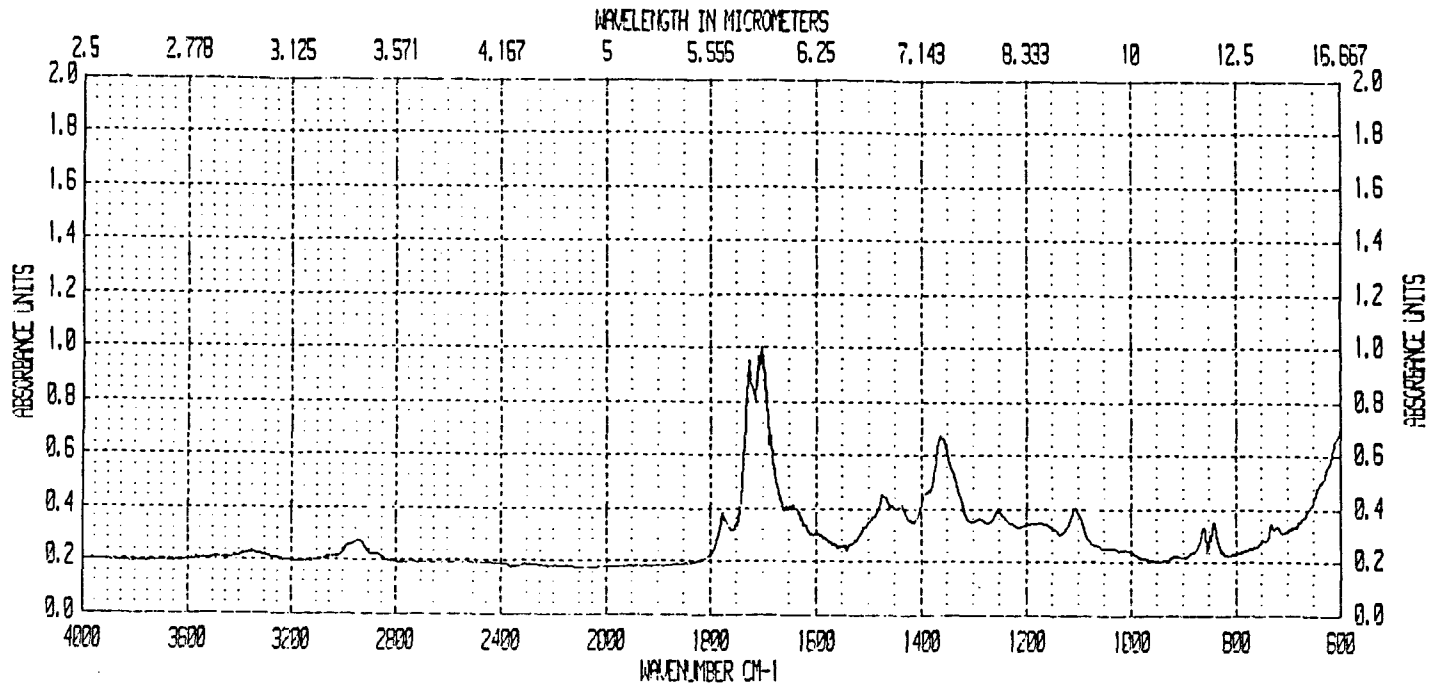
BECKMAN
ABSORBANCE UNITS
WAVELENGTH IN MICROMETERS
WAVENUMBER CM-1
t=90 min. @240°C
240/90
AT 240C FOR 90 MIN
4000.93
401.12
30 scans
0.2196

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
260/0	4	no	4000.93	401.12	30 scans	0.1927
	260C 0 TIME					



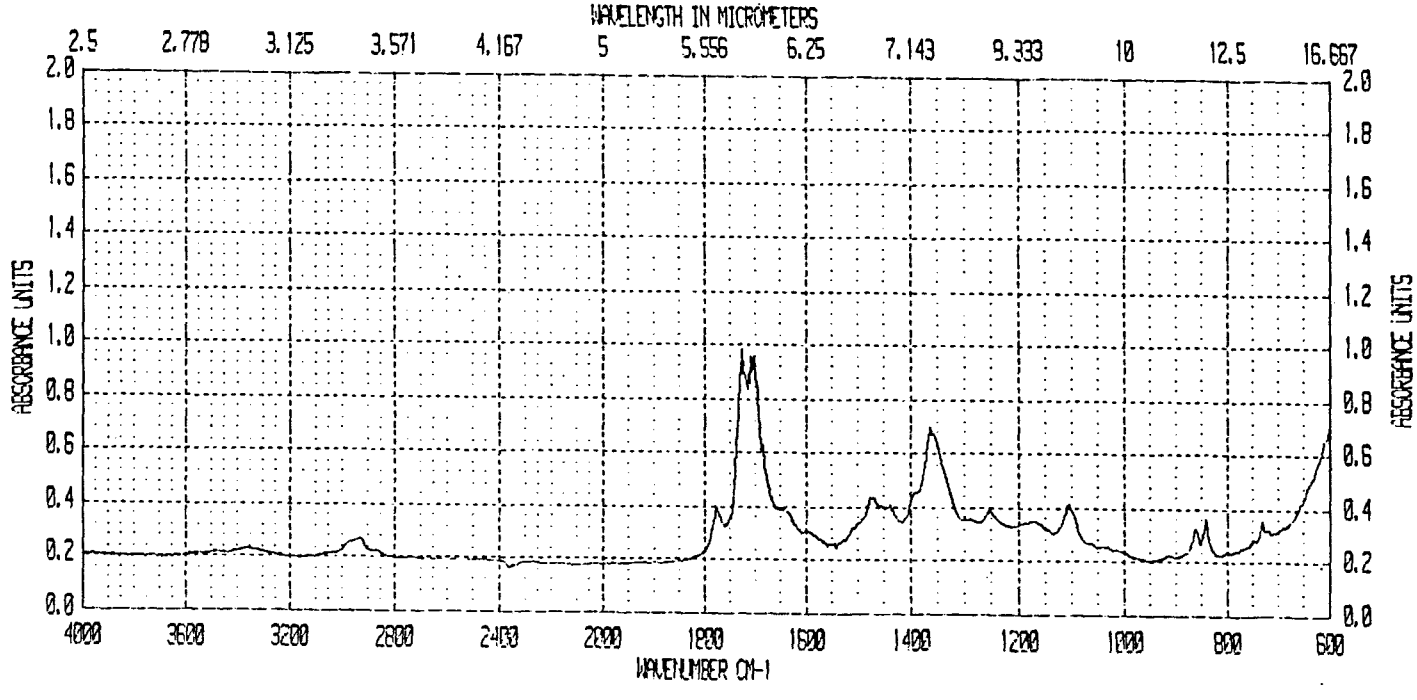
t=0 min @260°C

Scan Name	Resolu.	Apodized	Start	End	Scan time	First y
260/5	4 260C FOR 5 MIN	no	4000.93	401.12	30 scans	0.2029



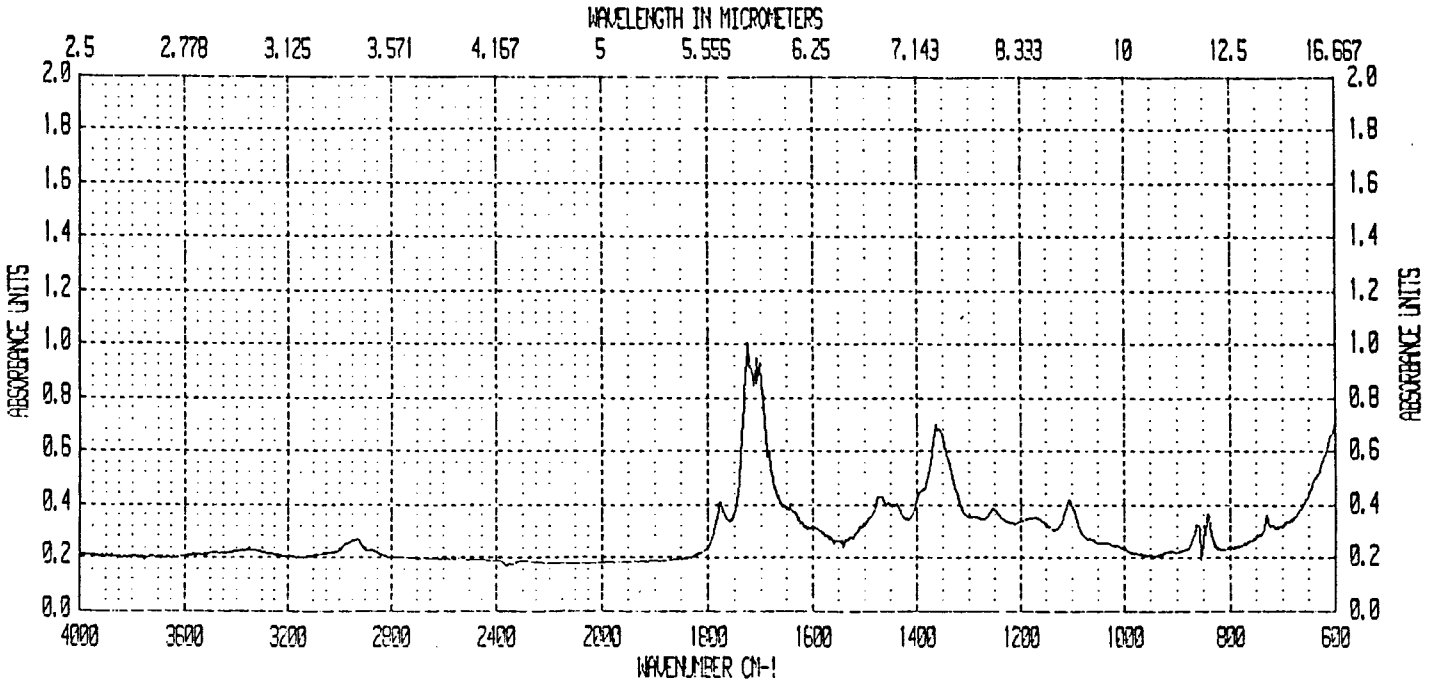
t=5 min. @260°C

Scan Name	Resolu	Apodized	Start	Clip	Scan Time	First y
260/1µ	4 260C FOR 10 MIN	no	4000.93	401.12	30 scans	0.2075



t=10 min. @260°C

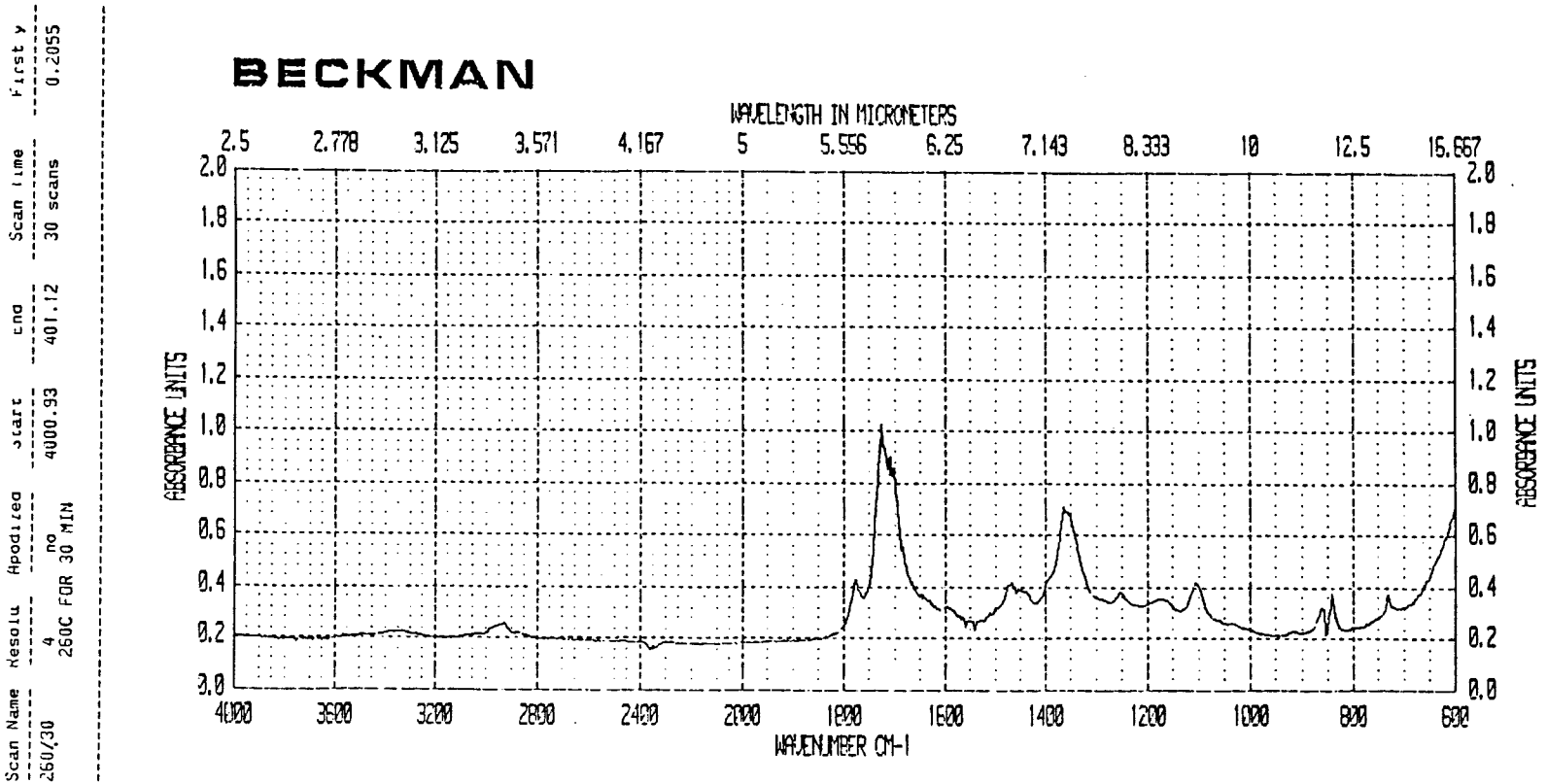
Scan Name	Resolu.	Apodized	Start	End	Scan Time	First y
260/15	4 260C FOR 15 MIN	no	4000.33	401.12	30 scans	0.2103



t=15 min. @260°C

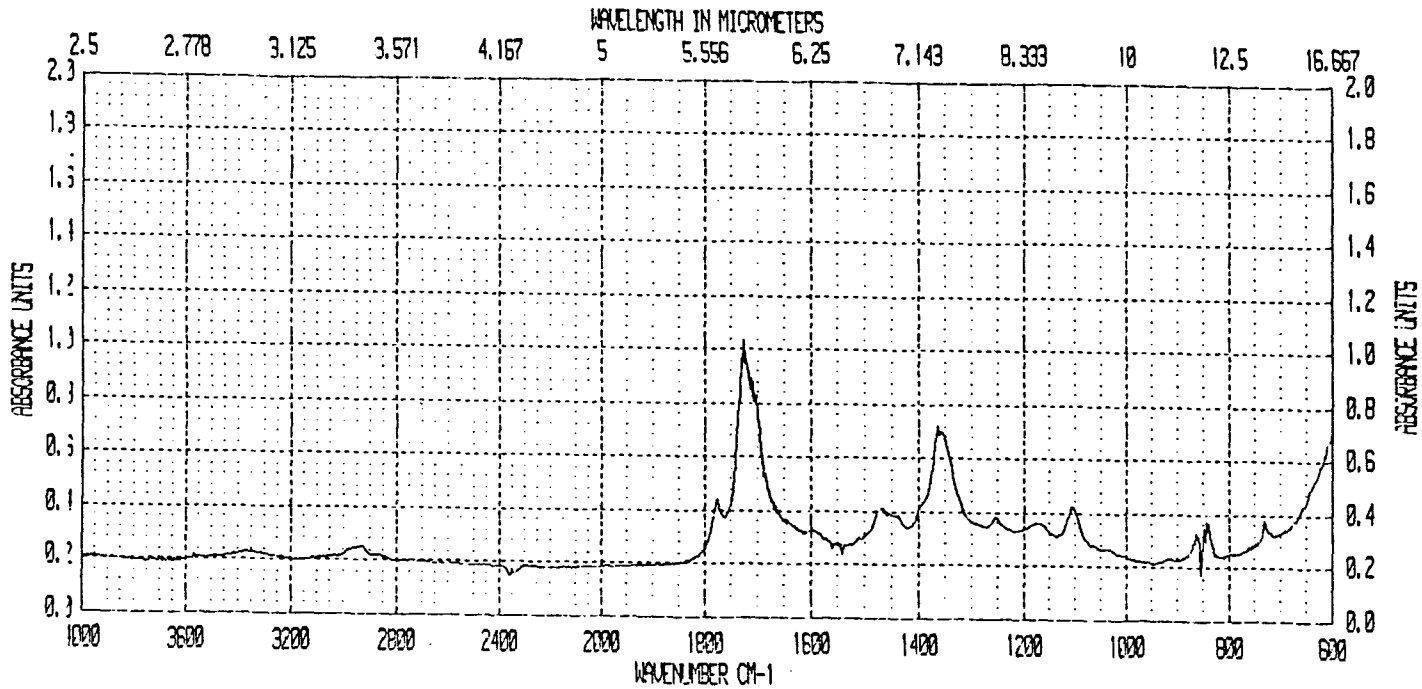
BECKMAN
ABSORBANCE UNITS
WAVELENGTH IN MICROMETERS
WAVENUMBER CM-1
ABSORBANCE UNITS
2.5 2.778 3.125 3.571 4.167 5 5.555 6.25 7.143 8.333 10 12.5 16.667
4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600
2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0
Scan Name 260/20
Resolu 4
Hpodized no
260C FOR 20 MIN
Start 4000.93
End 401.12
Scan time 30 scans
Filter y 0.3129

t=20 min. @260°C

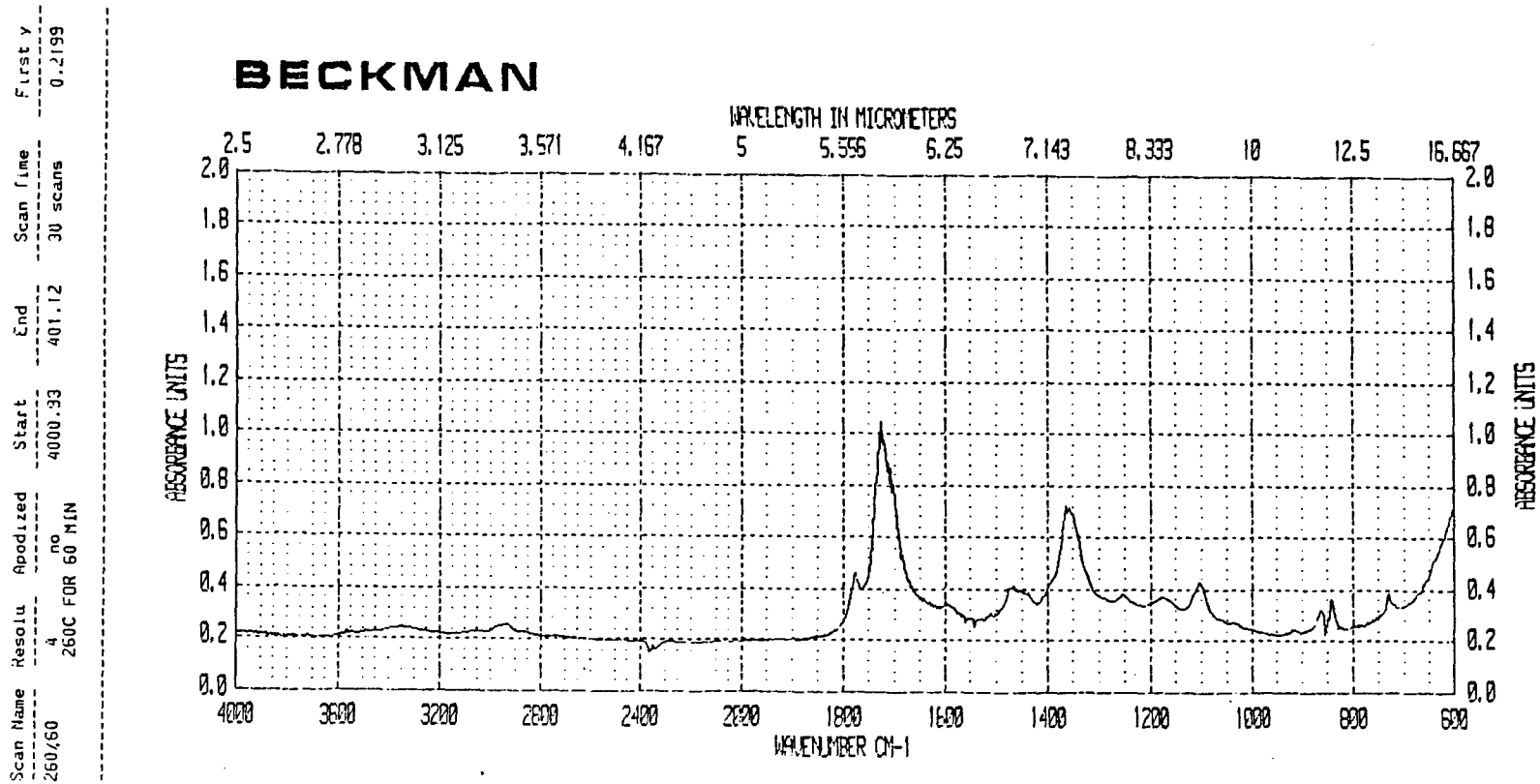

BECKMAN
WAVELENGTH IN MICROMETERS
2.5 2.778 3.125 3.571 4.167 5 5.556 6.25 7.143 8.333 10 12.5 15.667
ABSORBANCE UNITS
2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0
4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600
WAVENUMBER CM-1
Scan Name Resolu Apodized Start End Scan time First y
260/30 4 no 4000.93 401.12 30 scans 0.2055
260C FOR 30 MIN

t=30 min. @260°C

Scan Name	Resolu	Apodized	Start	End	Scan time	First y
260/40	4	no	4000.93	401.12	30 scans	0.2083
	260C FOR 40 MIN					

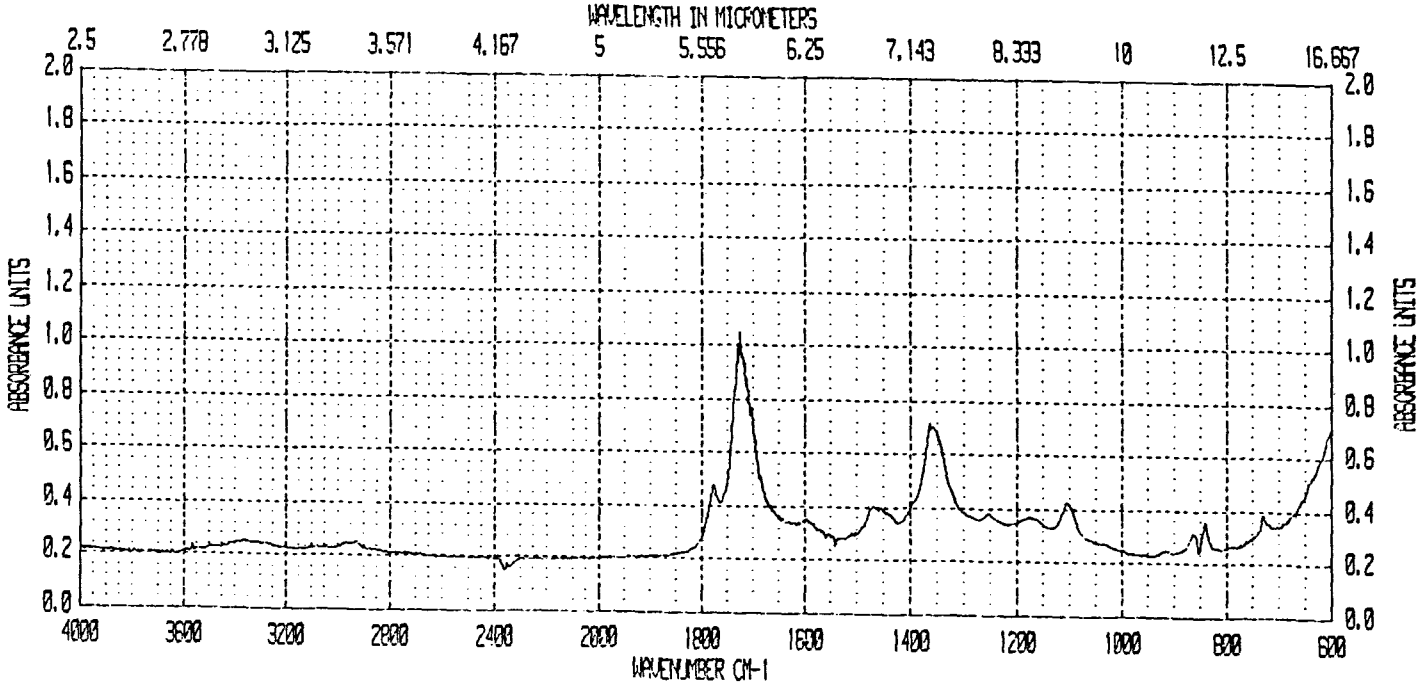


t=40 min. @260°C


BECKMAN
WAVELENGTH IN MICROMETERS
2.5 2.778 3.125 3.571 4.167 5 5.556 6.25 7.143 8.333 10 12.5 16.667
ABSORBANCE UNITS
2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0
4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600
WAVENUMBER CM-1
Scan Name 260/60
Resolu 4
Apodized no
260C FOR 60 MIN
Start 4000.33
End 401.12
Scan Time 30 scans
First y 0.2199

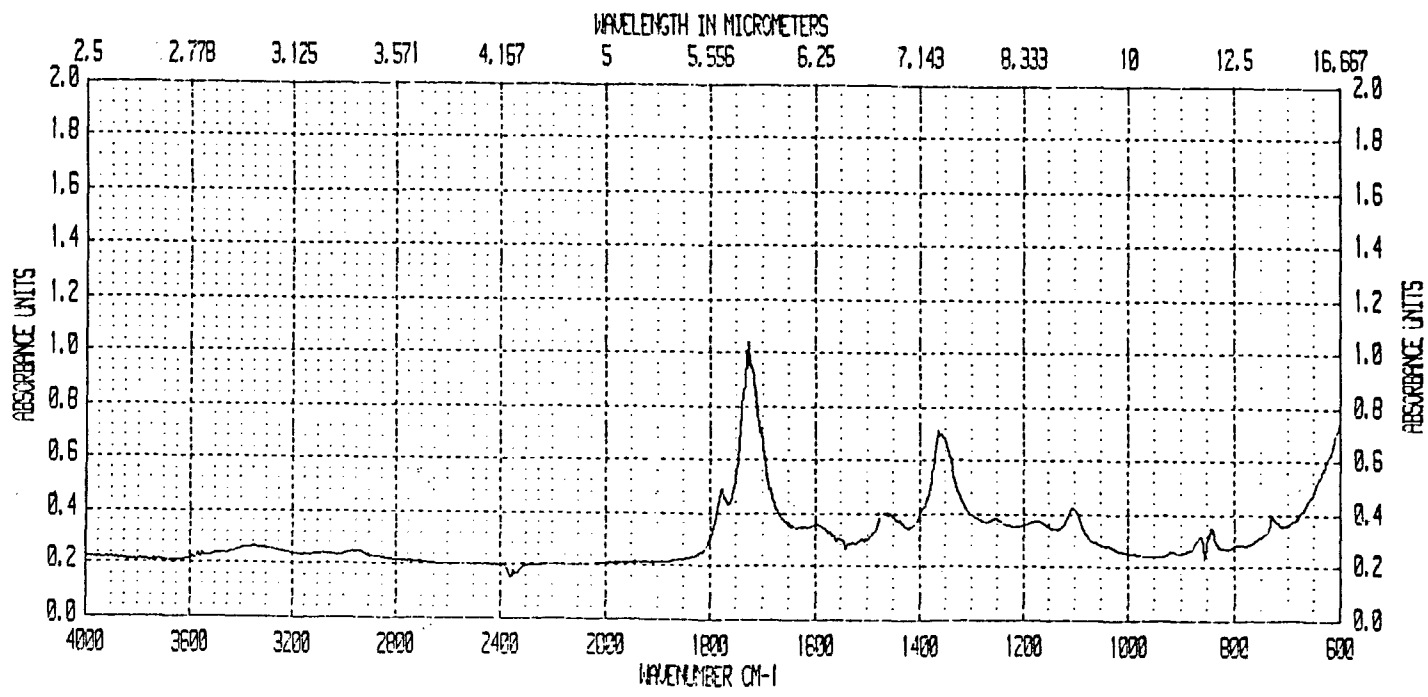
t=60 min. @260°C

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
260/90	4 260C FOR 90 MIN	no	4000.93	401.12	30 scans	0.2188



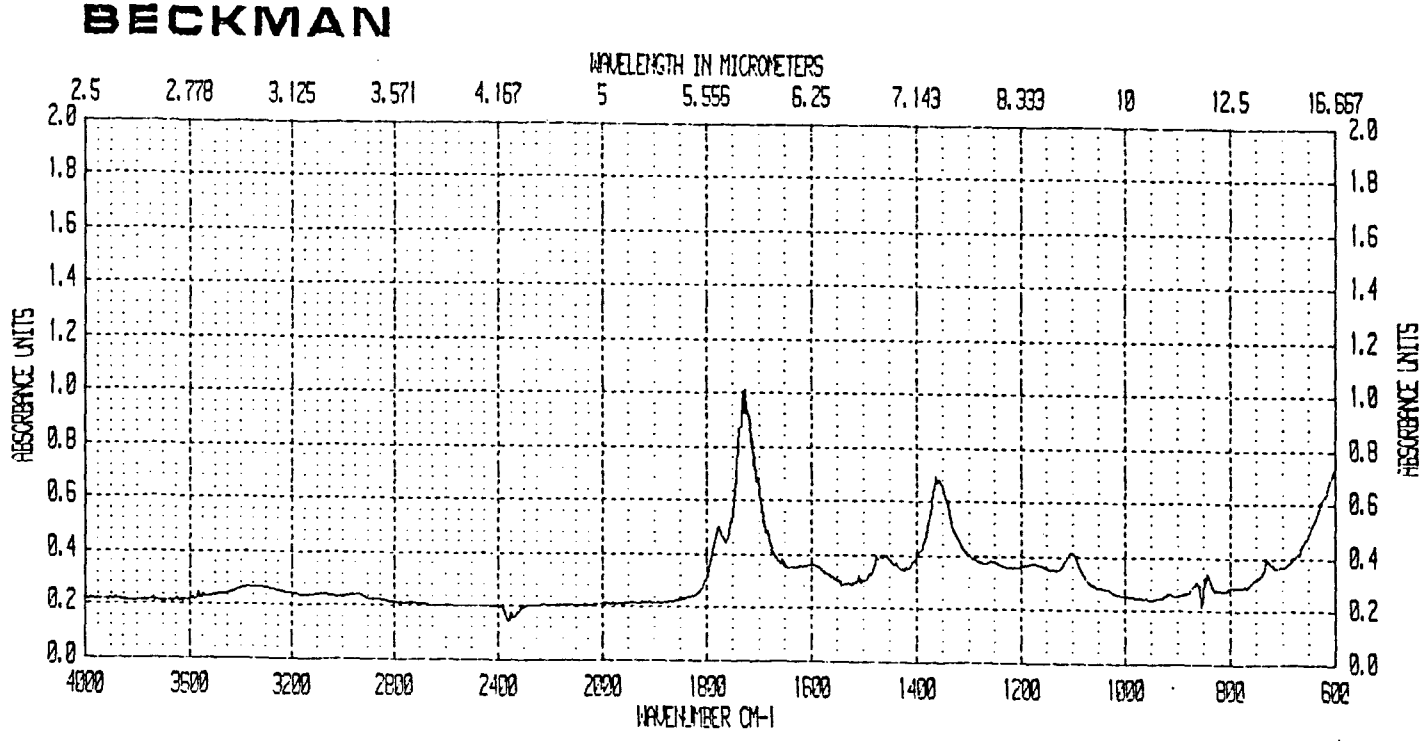
t=90 min. @260°C

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
260/150	4 260C FOR 150 MIN	no	4000.93	401.12	30 scans	0.2240



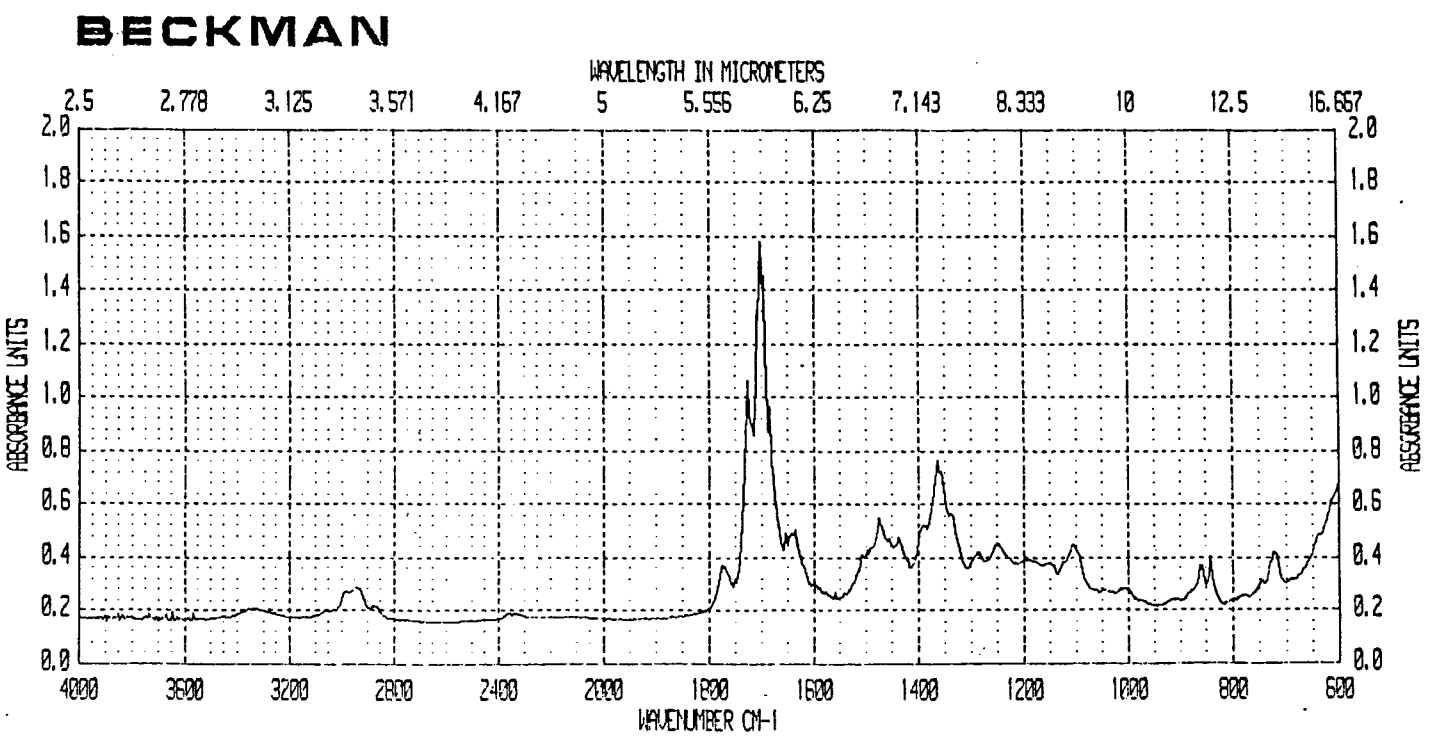
t=150 min. @260°C

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
260/240	4	no	4000.93	401.12	30 scans	0.2211
	260C FOR 240 MIN					

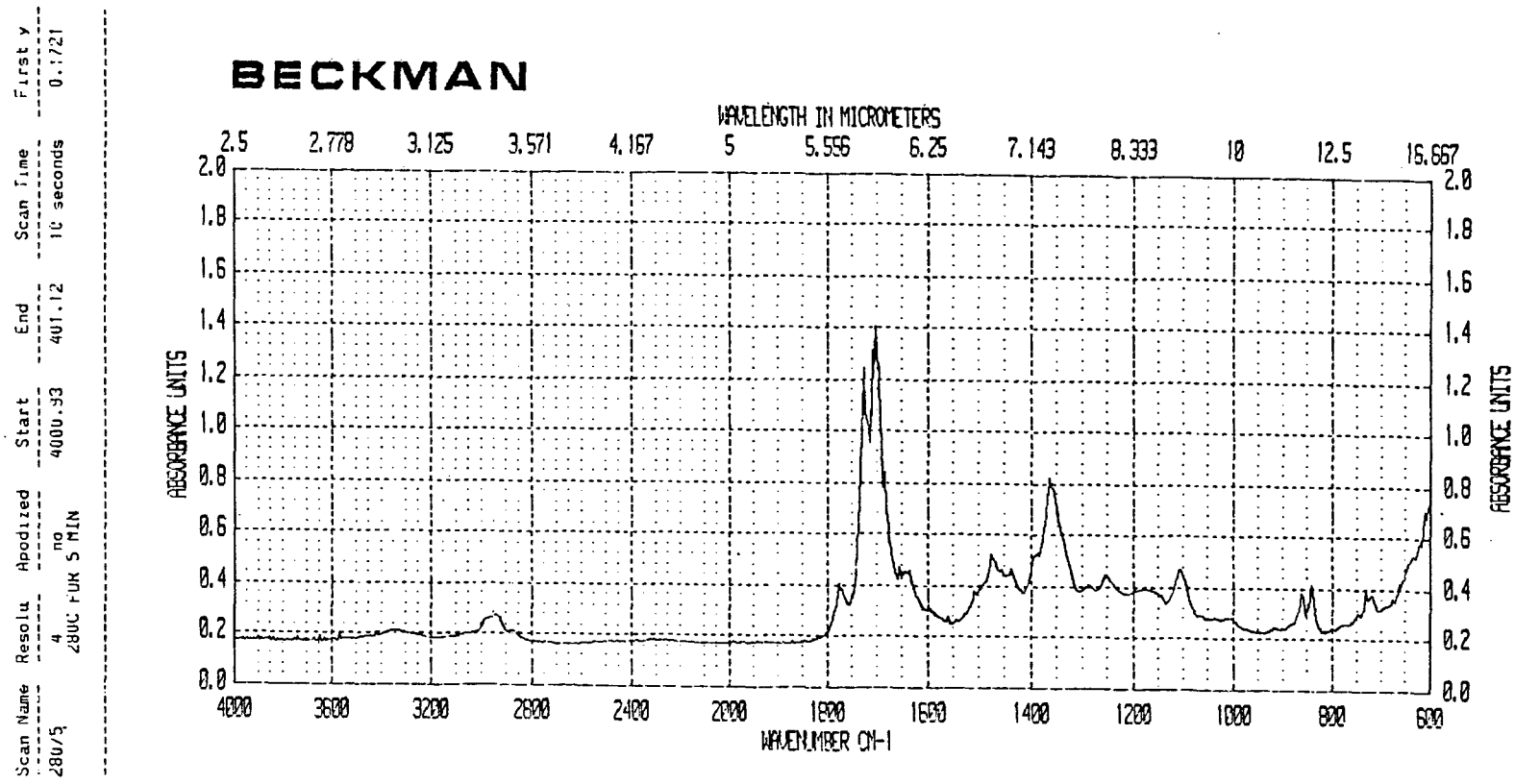


t=240 min. @260°C

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
280/0	4 280C FOR T=0 MIN	no	4000.93	401.12	9 seconds	0.1706



t=0 min. @280°C


BECKMAN
WAVELENGTH IN MICROMETERS
2.5 2.778 3.125 3.571 4.167 5 5.556 6.25 7.143 8.333 10 12.5 16.667
ABSORBANCE UNITS
2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0
4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600
WAVENUMBER CM-1
Scan Name Resolu Apodized Start End Scan Time First y
280/5 4 no 4000.93 401.12 10 seconds 0.1721
280C FOR 5 MIN

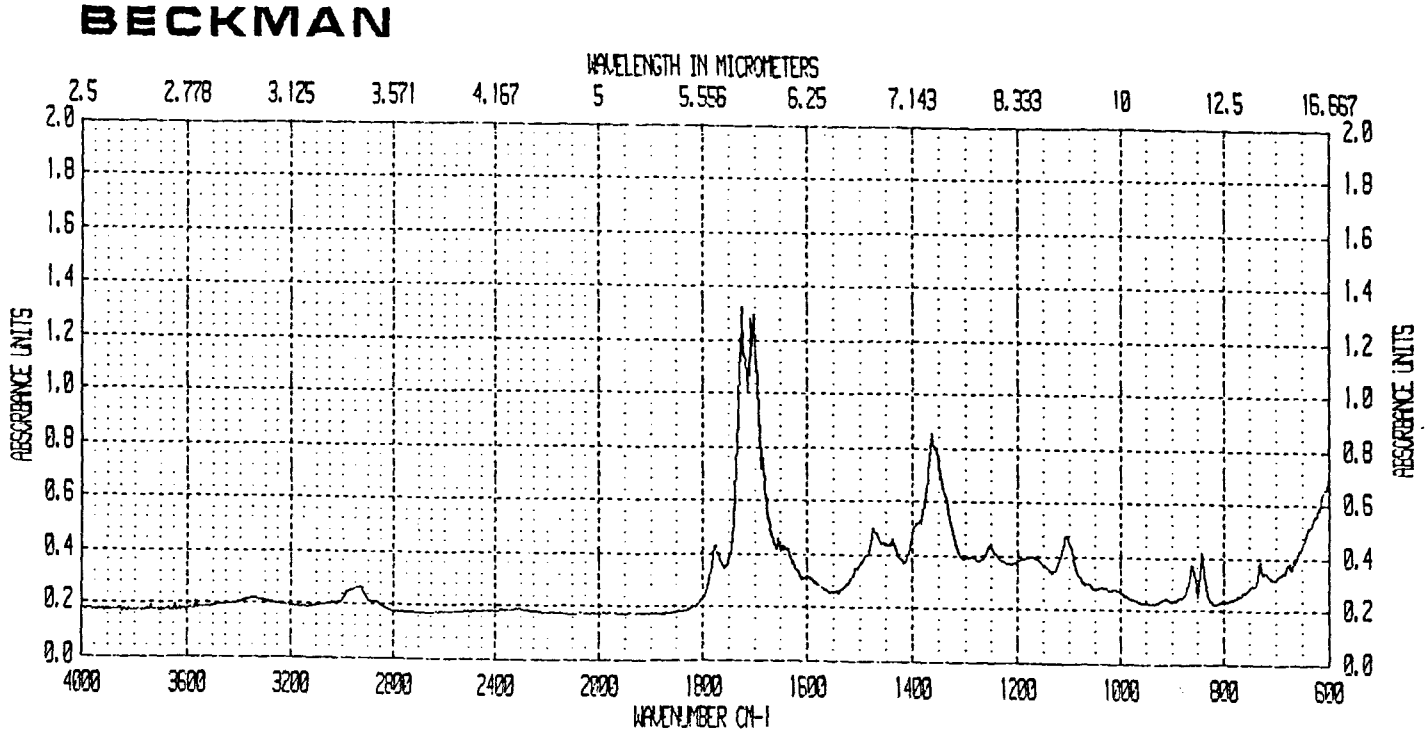
t=5 min. @280°C

t=10 min. @280°C

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
280/10	4	no	4000.93	401.12	11 seconds	0.17552

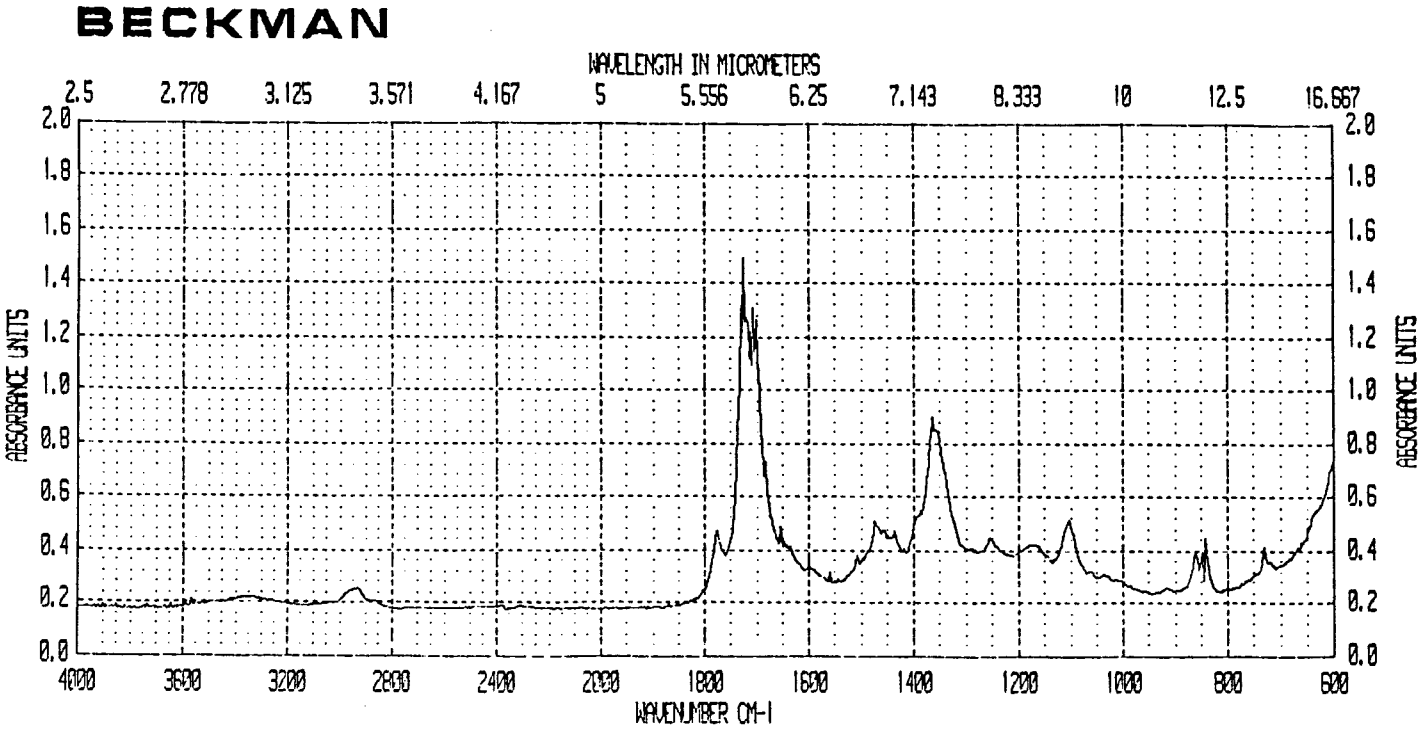
280C FOR 10 MIN

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
280/15	4 280C FOR 15 MIN	no	4000.93	401.12	10 seconds	0.1770



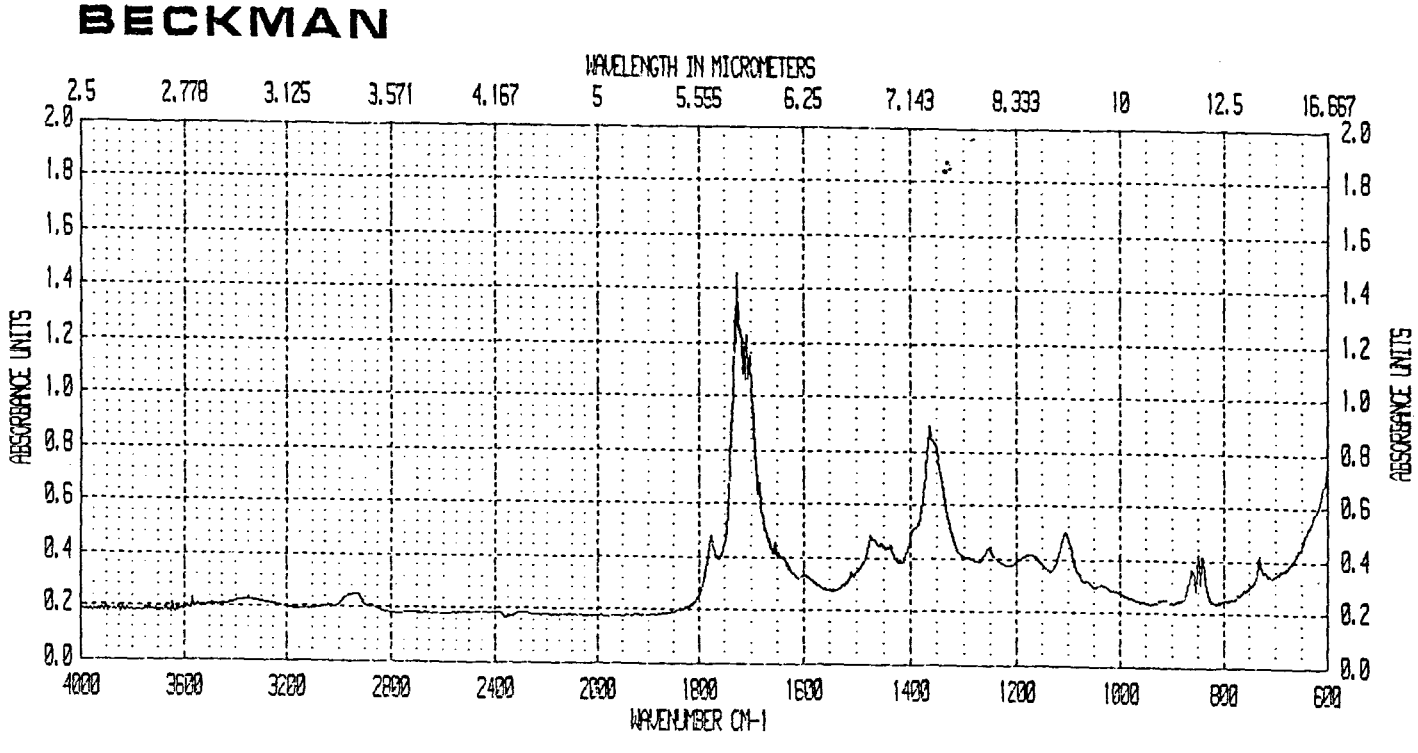
t=15 min. @280°C

Scan Name	Resolu	Apodized	Start	End	Scan time	First y
280/30	4	no	4000.93	401.12	10 seconds	0.1810
	280C FÜR 30 MIN					

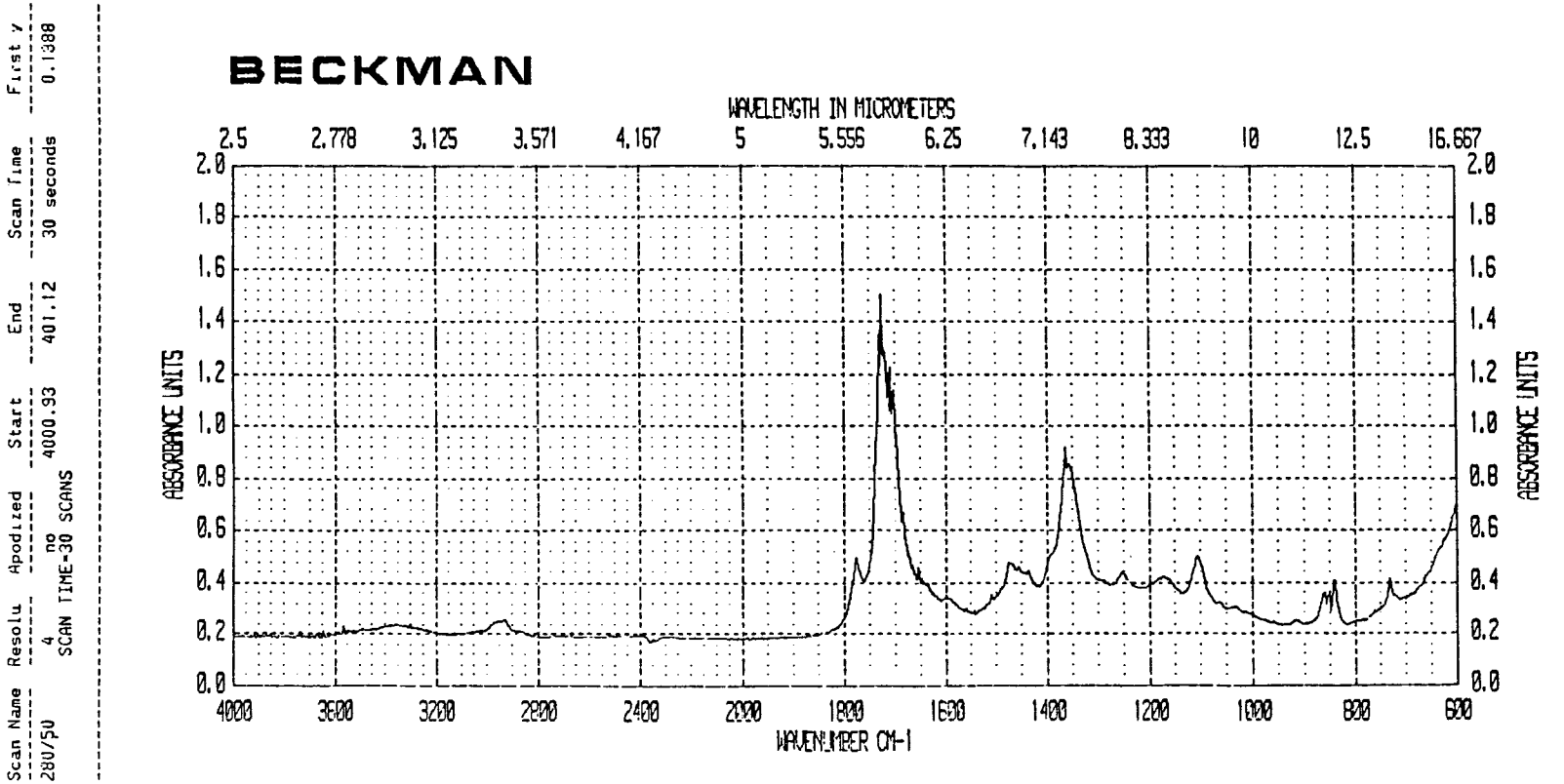


t=30 min. @280°C

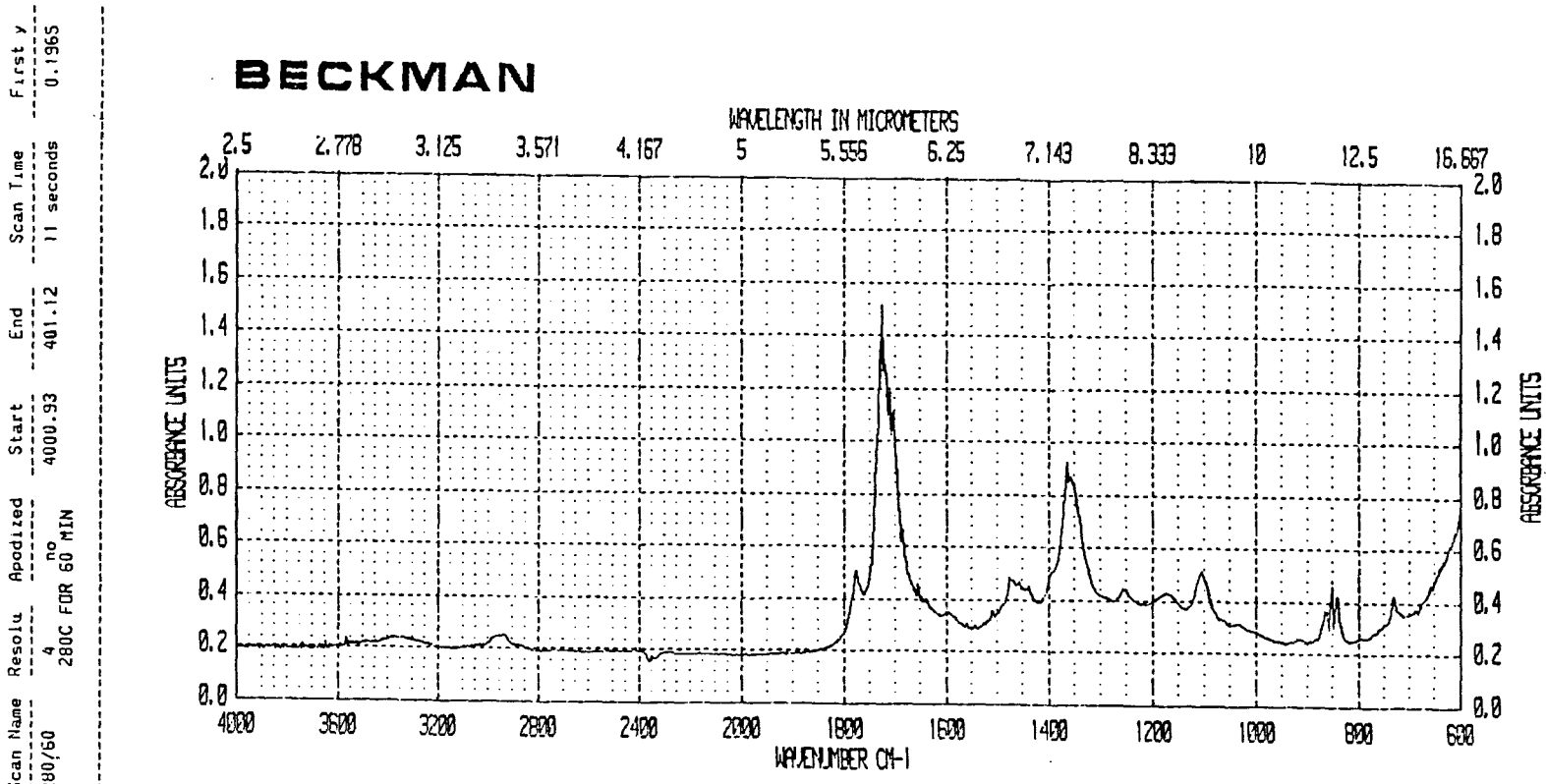
Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
280/4U	4 280C FOR 40 MIN	no	4000.93	401.12	11 seconds	0.1863



t=40 min. @280°C

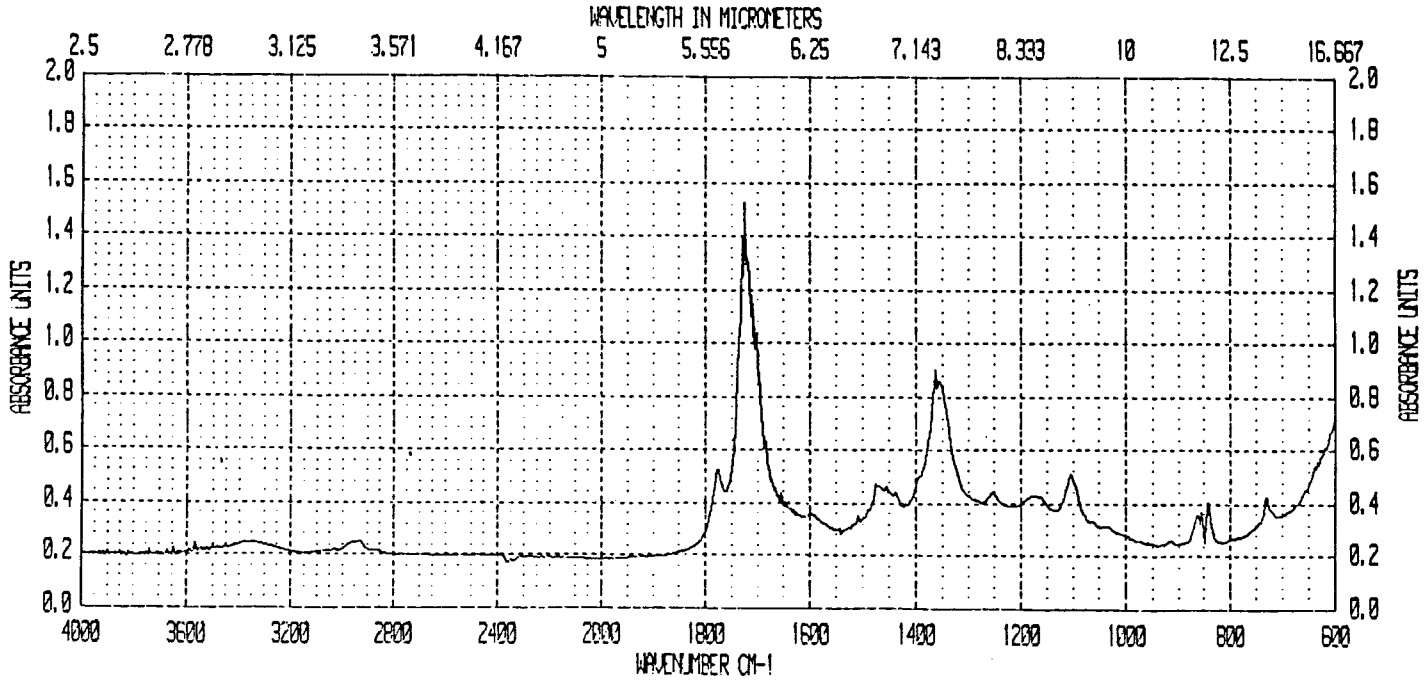

BECKMAN
WAVELENGTH IN MICROMETERS
2.5 2.778 3.125 3.571 4.167 5 5.556 6.25 7.143 8.333 10 12.5 16.667
ABSORBANCE UNITS
2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0
4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600
WAVENUMBER CM-1
Scan Name Resolu Apodized Start End Scan Time First Y
280/5U 4 no 4000.93 401.12 30 seconds 0.1388
SCAN TIME=30 SCANS

t=50 min. @280°C


BECKMAN
WAVELENGTH IN MICROMETERS
2.5
2.778
3.125
3.571
4.167
5
5.556
6.25
7.143
8.333
10
12.5
16.667
ABSORBANCE UNITS
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
WAVENUMBER CM-1
Scan Name
280/60
Resolu
4
Apodized
no
280C FOR 60 MIN
Start
4000.93
End
401.12
Scan Time
11 seconds
First y
0.1965

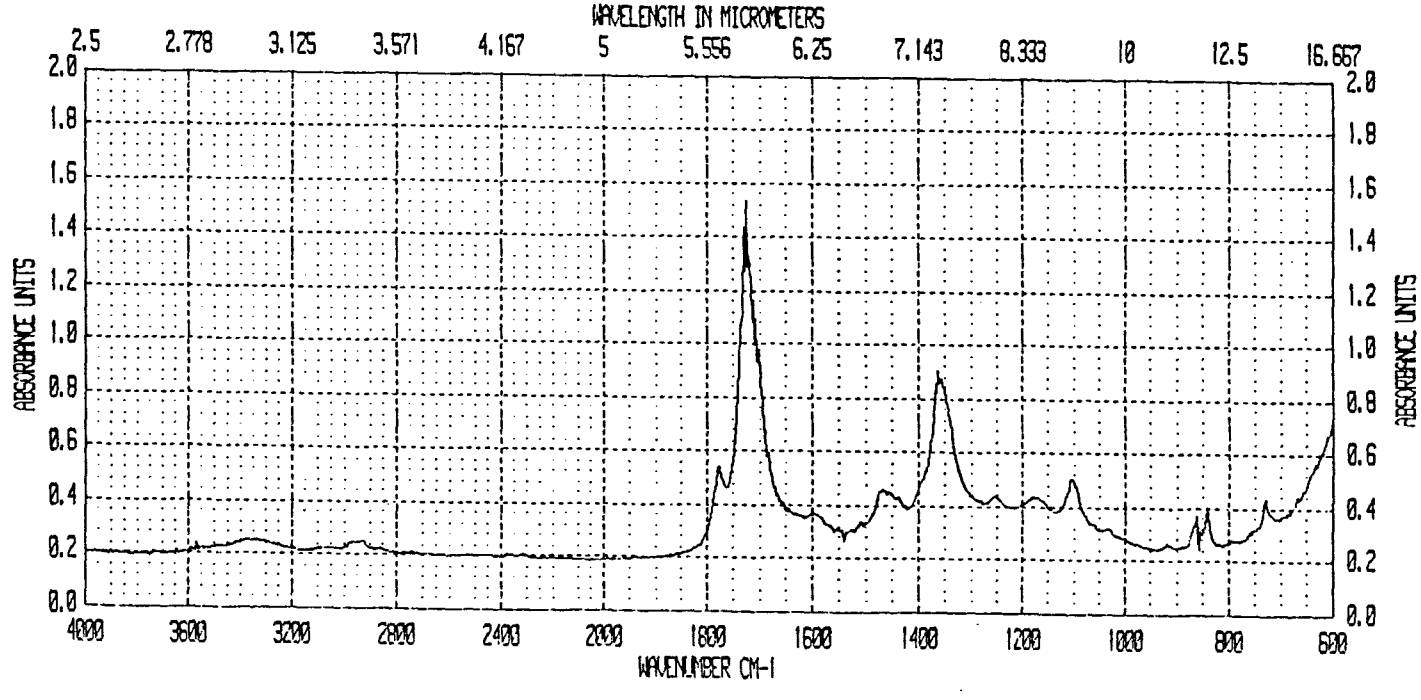
t=60 min. @280°C

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
280/90	4	no	4000.93	401.12	9 seconds	0.2016
	280C FOR 90 MIN					



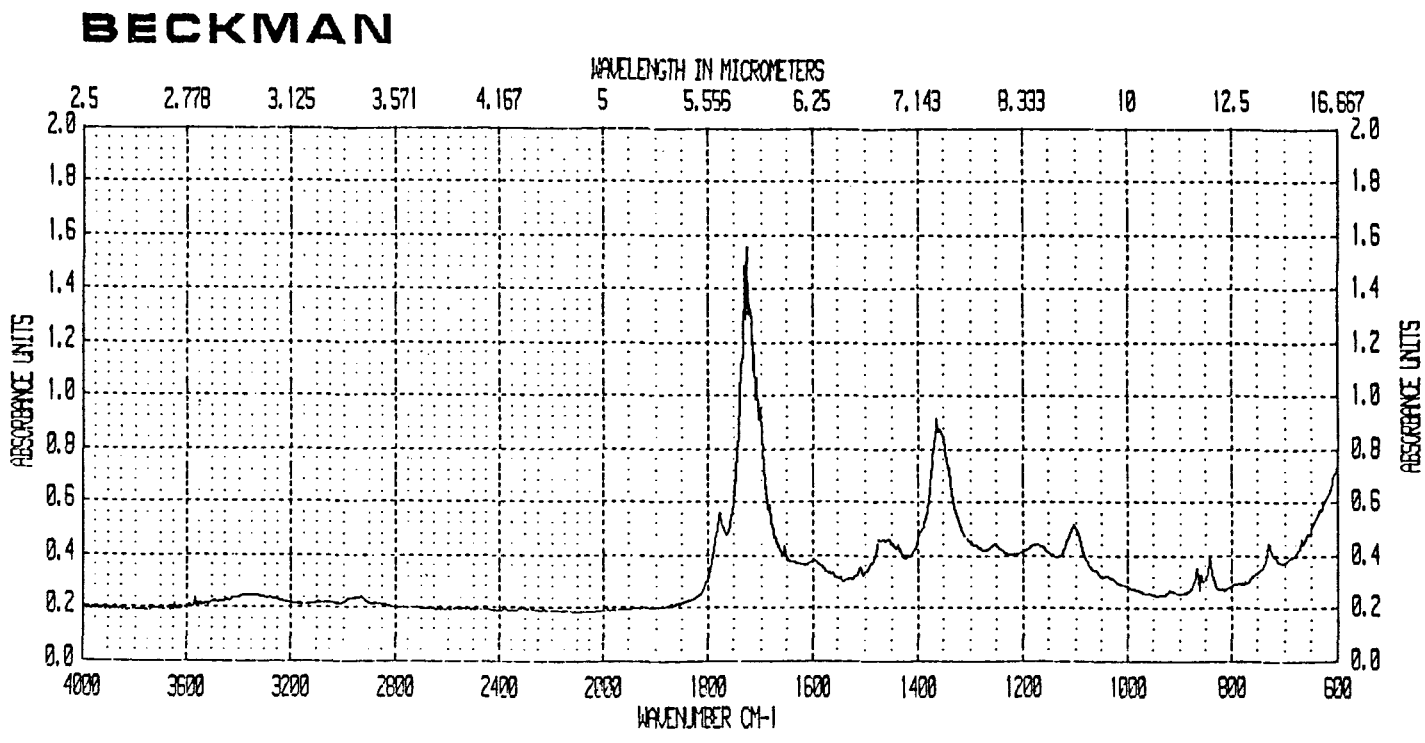
t=90 min. @280°C

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
280/130	4	no	4000.93	401.12	10 seconds	0.2011
	280C FOR 130 MIN					



t=130 min. @280°C

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
280/180	4	no	4000.93	401.12	10 seconds	0.1950
	280C FOR 180 MIN					



t=180 min. @280°C

APPENDIX D

Subtraction Spectra from FTIR for PAA/DNI-3A

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESULT	4	no	3998.36	401.12	30 scans	3.0103

No additional information

3400 - 3000

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESOLT	4	no	3998.36	401.12	30 scans	3.0384
	No additional information					

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESULT	4	no	3998.36	401.12	30 scans	3.0384

No additional information

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESULT	4	no	3998.36	401.12	30 scans	3.0384

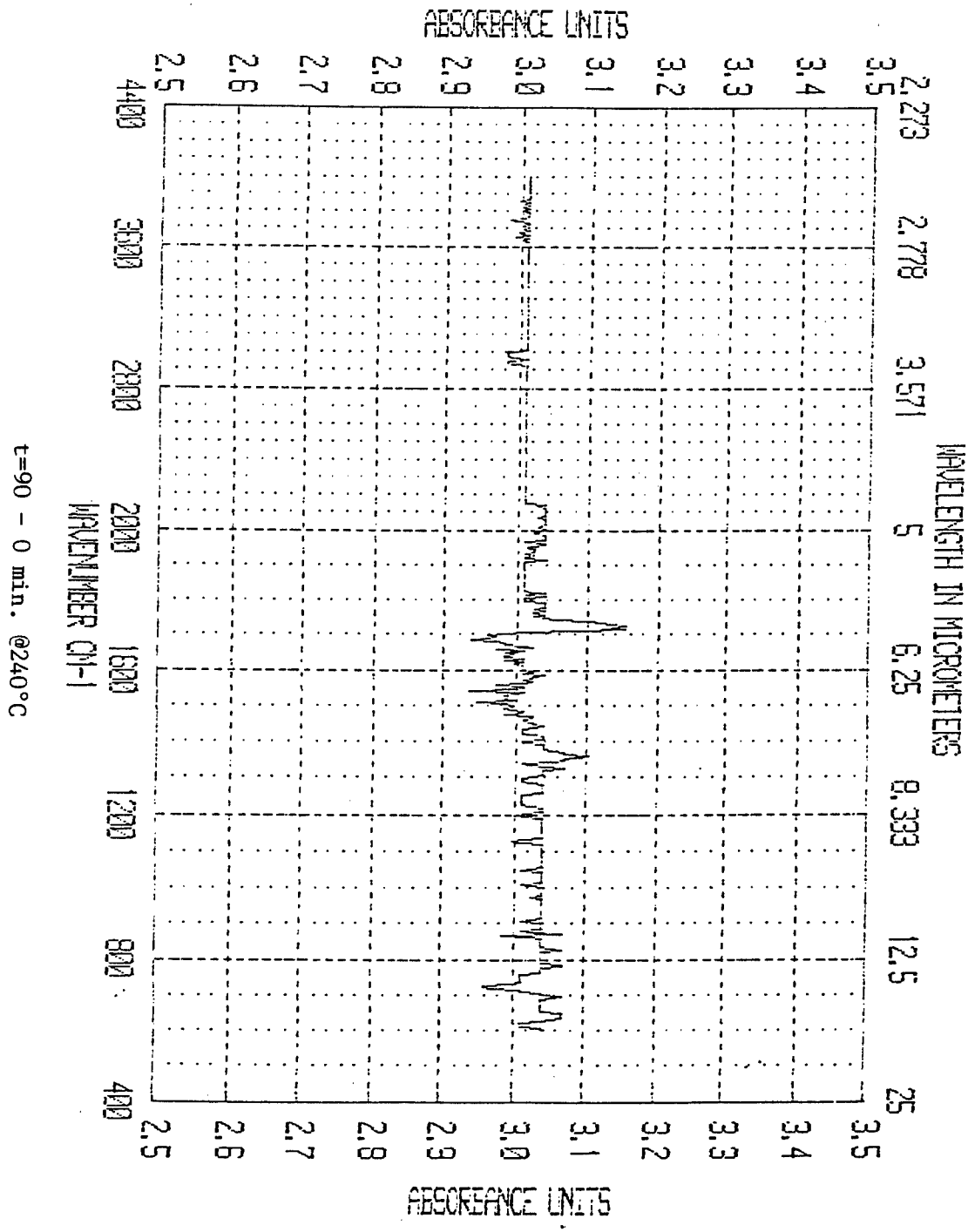
No additional information

Note - adjust

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESULT	4	no	3998.36	401.12	30 scans	3.0103

No additional information

240/90 - 240/0



Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESULT	4	no	3998.36	401.12	30 scans	3.0103

No additional information

Mols - mols

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESOLT	4	no	3598.36	401.12	30 scans	3.0324

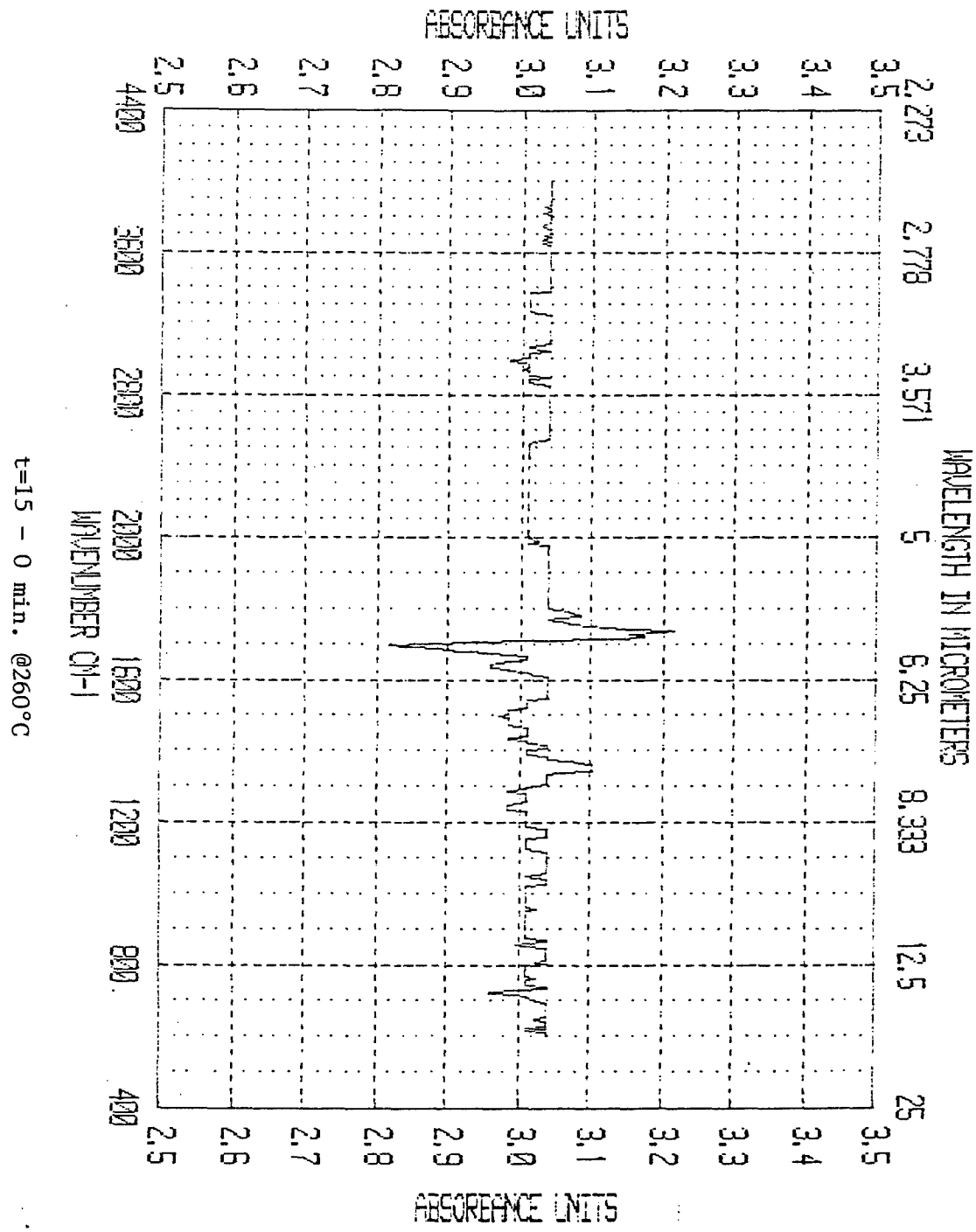
No additional information

20% - 20%

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESULT	4	no	3398.36	401.12	30 scans	3.0384

No additional information

260/15 - 260/0



Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESULT	4	no	5998.36	401.12	30 scans	3.0384

No additional information

260°C - 20°C

t=30 -0 min. @260°C

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESULT	4	no	3998.36	401.12	30 scans	3.0384

No additional information

30%/0 - 20%/0

RESULT	Scan Name
No additional information	
4	Resolu
no	Apodized
3998.36	Start
401.12	End
30 scans	Scan Time
3.0384	First y

%/oz - oz/oz

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESULT	4	no	3998.36	401.12	30 scans	3.0384

No additional information

%o/o - %o/o

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESULT	4	no	3998.36	401.12	30 scans	3.038e4

No additional information

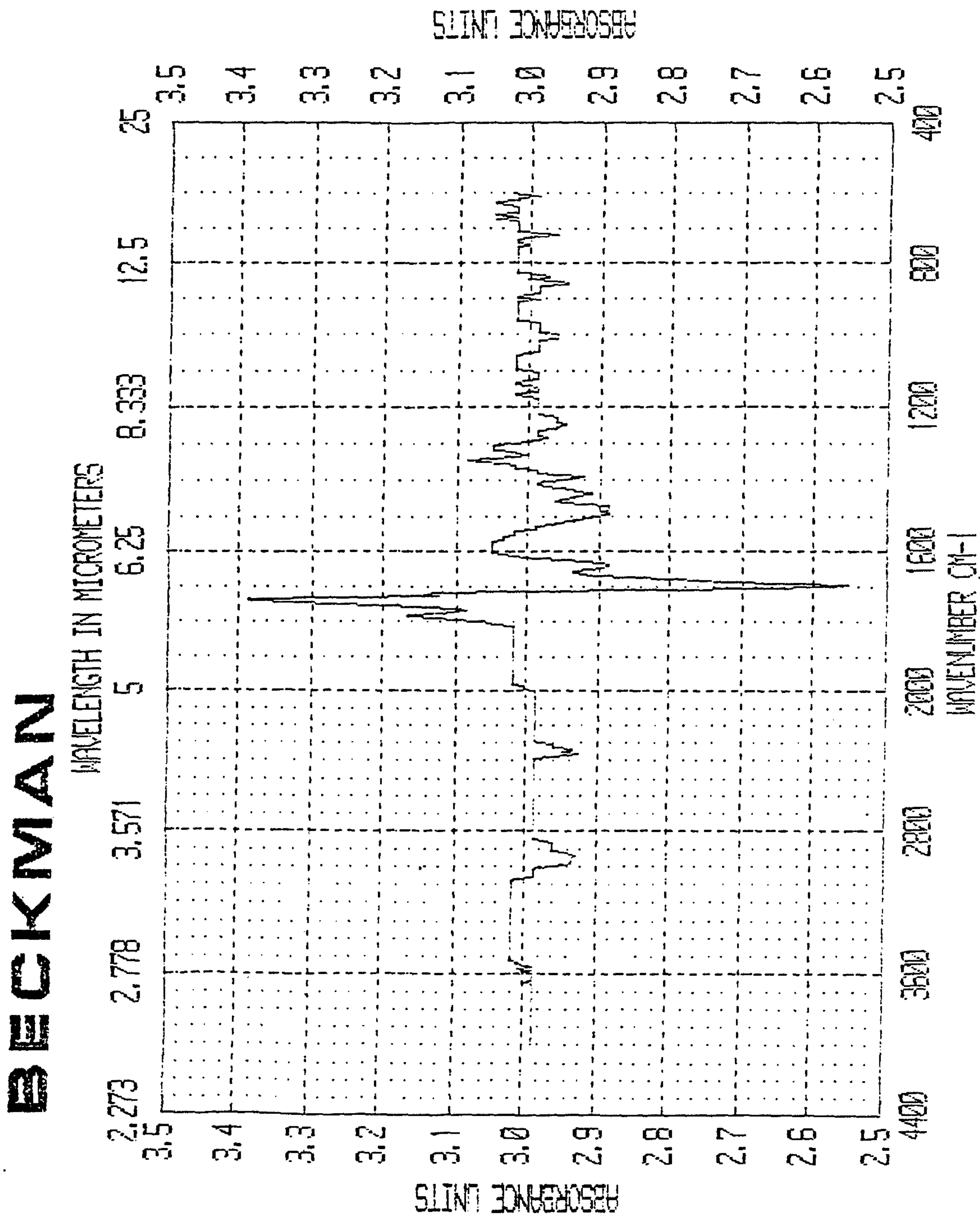
%o/%o - %o/%o

t=150 - 0 min. @260°C

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESULT	4	no	3998.36	401.12	30 scans	3.0384

No additional information

%o/so . %o/so



t=240 - 0 min. @260°C

Scan Name	Resolu	Apodized	Start	End	Scan Time	First Y
RESULT	4	no	3998.36	401.12	30 scans	3.0384

No additional information

240/240 - 260.

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESULT	4	no	3998.36	401.12	10 seconds	3.0:03

No additional information

280/5 - 280/

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESULT	4	no	3998.36	401.12	11 seconds	3.0103

No additional information

280°C - 280°C

t=15 - 0 min. @280°C

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESULT	4	no	3998.36	401.12	10 seconds	3.0103

No additional information

280/15 - 280/0

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESULT	4	no	3998.36	401.12	10 seconds	3.0384

No additional information

%/sec - %/sec

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESULT	4	no	3998.36	401.12	11 seconds	3.0384

No additional information

280/40 - 280/0

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESULT	4	no	3998.36	401.12	30 seconds	3.0384

No additional information

280/50 - 280/0

RESULT

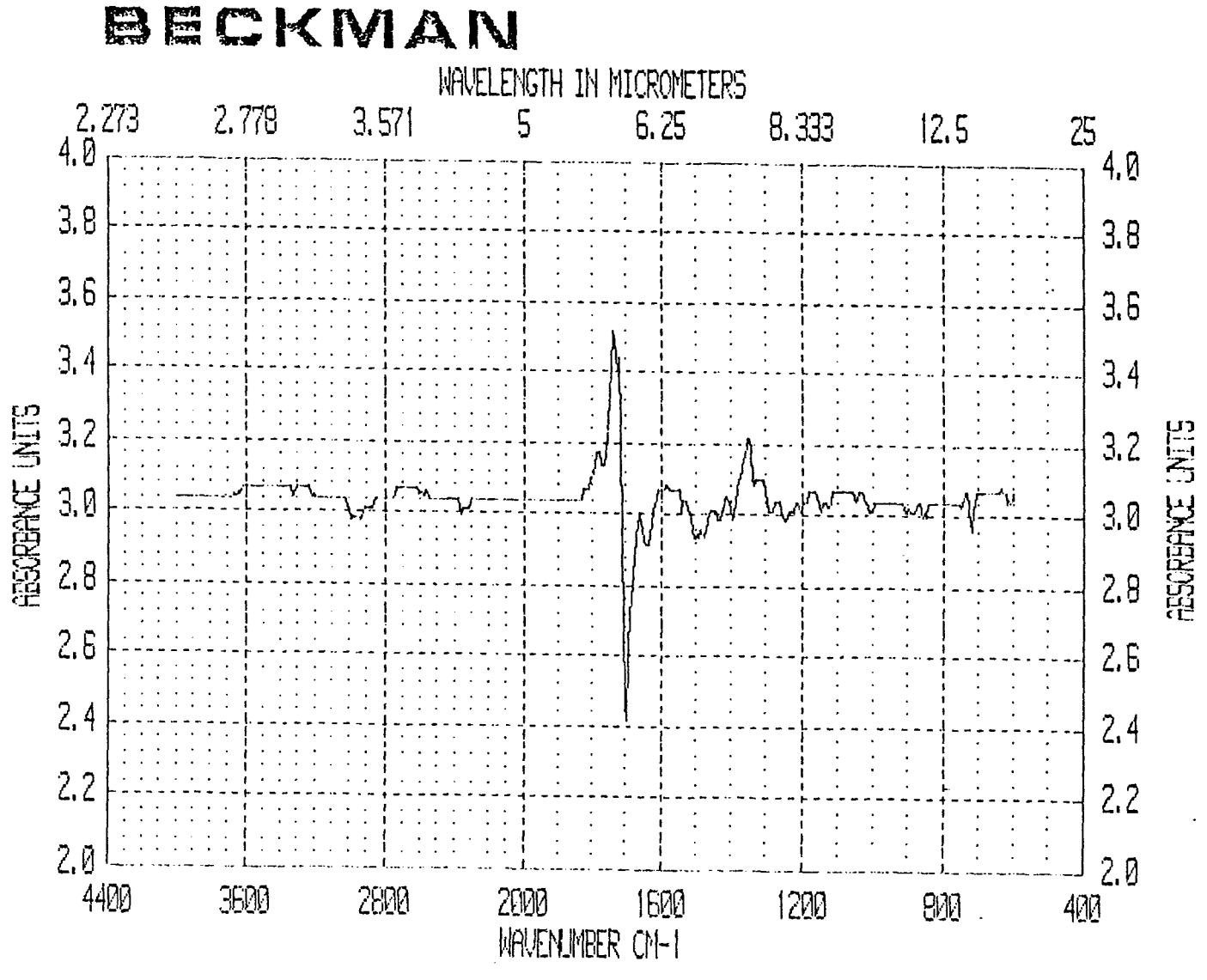
Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
	4	no	3998.36	401.12	11 seconds	3.0384

No additional information

28%o - 28%

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESULT	4	no	3998.36	401.12	9 seconds	3.0384
	No additional information					

280/90 - 280/.



t= 90 - 0 min. @280°C

Scan Name	Resolu	Apodized	Start	End	Scan Time	First y
RESULT	4	no	3998.35	401.12	10 seconds	3.0384

No additional information

280/130 - 280%

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